

**A Review of Literature Related to Oil Spill Dispersants  
Especially Relevant to Alaska  
2002-2008**

for

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by

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## Abstract

This report is a review of the literature on oil spill dispersants published from 2002 to August, 2008. The report identifies and summarizes recent advances in dispersant effectiveness, toxicity, and biodegradation.

The prime motivation for using dispersants is to reduce the impact of oil on shorelines, thus the application must be successful and effectiveness high. As some oil would come ashore, discussion remains on what effectiveness is required to significantly reduce the shoreline impact. A major issue is the actual effectiveness during spills so that these values can be used in estimates for the future. The second motivation for using dispersants is to reduce the impact on birds and mammals on the water surface. The benefits of using dispersants to reduce impacts on wildlife still remain unknown. The third motivation for using dispersants is to promote the biodegradation of oil in the water column. The effect of dispersants on biodegradation is still a matter of dispute. Some papers state that dispersants inhibit biodegradation others indicate that dispersants have little effect on biodegradation. The most recent papers, however, confirm that inhibition is a matter of the surfactant in the dispersant itself and the factors of environmental conditions. It is clear, on the basis of current literature that the surfactants in some of the current dispersant formulations can inhibit biodegradation. No enhancement of biodegradation was clearly shown in any recent studies.

Effectiveness remains a major issue with oil spill dispersants. It is important to recognize that many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water. The most important of these is the composition of the oil, followed closely by sea energy. It is equally important to note that **the only thing that is important is effectiveness on real spills at sea**. More emphasis might be put on monitoring to provide reliable information for assessment and modeling.

The results of dispersant toxicity testing are similar to that found in previous years, namely that dispersants vary in their toxicity to various species, however, dispersant toxicity is less than the toxicity of dispersed oil, by most tests. Of the recent toxicity studies of dispersed oil, most researchers found that chemically-dispersed oil was more toxic than physically-dispersed oil. About half of these found that the cause for this was the increased PAHs, typically about 5 to 10 times, in the water column. Others noted the increased amount of total oil in the water column. Some noted the damage to fish gills caused by the increased amount of droplets. Some researchers noted that the toxicity of chemically-dispersed oil was roughly equivalent to physically-dispersed oil.

The interaction of droplets, particularly chemically-dispersed droplets appears to be an important facet of oil fate. It appears that high concentrations of sediment will have significant effect on dispersed oil droplets and the formation of stable OMAs (Oil-Mineral-Aggregates). OMAs appear to be stable over time and sink slowly and sediment on the bottom. Oil spill dispersions themselves are not stable and dispersed oil will de-stabilize and rise to the surface. Half-lives of dispersions may be between 4 to 24 hours.

During the time period covered by this review, the U.S. National Academy of Sciences published a review of dispersants. This report is summarized here and contains many useful insights, summaries and recommendations.



## Executive Summary

### Overall

The literature on oil spill dispersants between 2001 and 2008 is extensive, consisting of more than 300 papers. The prime motivation for using dispersants is to reduce the impact of oil on shorelines. To accomplish this, the dispersant application must be highly successful and effectiveness high. As some oil would come ashore, there is much discussion on what effectiveness is required to significantly reduce the shoreline impact. A major issue that remains is the actual effectiveness during spills so that these values can be used in estimates for assessment and models.

The second motivation for using dispersants is to reduce the impact on birds and mammals on the water surface. As the NAS committee (2006) on dispersants notes, little or no research on this has been carried out anytime since the 1980's. The benefits or deleterious effects of using dispersants to reduce impacts on wildlife still remain unknown.

The third motivation for using dispersants is to promote the biodegradation of oil in the water column. The effect of dispersants on biodegradation is still a matter of discussion. There are a number of contradictory papers stating that dispersants inhibit biodegradation others indicate that dispersants have little effect on biodegradation. The most recent papers, however, confirm that inhibition is a matter of the surfactant in the dispersant itself and the factors of environmental conditions. What is very clear at this time is that the surfactants in some of the current dispersant formulations can either inhibit or leave biodegradation unaffected. In recent studies it was never shown that dispersants clearly enhanced biodegradation. Further, there are issues about the biodegradability of the surfactant themselves and this fact can confound many tests of dispersed oil biodegradation. An important issue that rarely is discussed is that oil-degrading bacteria, largely live on the water surface, where they would feed on similar natural hydrocarbons in the absence of spills. Another serious question is that of time scale. Biodegradation takes place over weeks, months and years compared to dispersion half lives of 12 to 36 hours.

During the time period covered by this review, the U.S. National Academy of Sciences published a review of dispersants. This report is summarized here and contains many useful insights, summaries and recommendations.

### Effectiveness Testing Overall

Effectiveness remains a major issue with oil spill dispersants. It is important to recognize that many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water. The most important of these is the composition of the oil, followed closely by sea energy and the amount of dispersant applied. It is equally important to recognize that **the only thing that matters in the end is effectiveness on real spills at sea**. More emphasis might be put on monitoring this so the world has the real information for assessment and modeling.

Effectiveness issues are confounded by the simple fact that small or large scale tests show highly different results depending on how they are constructed and operated. Detailed scientific examination of any of these shows major deficiencies. More emphasis is needed on looking at the real results from real spills.

### **Laboratory Effectiveness Tests**

Bench scale testing continues to be widely used to evaluate the performance of dispersants and the physical and chemical mechanisms of oil dispersion. A major disadvantage is that it is difficult to scale the results of these tests to predict performance in the field. Several factors that are difficult to extrapolate include energy regimes, dilution due to advection and turbulent diffusion. Bench scale tests are very useful for determining the effectiveness of various dispersant-oil combinations, salinity, temperature effects, effects of oil composition and effects of oil weathering. It has been noted that many of the current tests may be too energetic as they yield results well above that obtained in older field tests.

### **Tank Testing**

Tank testing continued at high levels during the review time period. Tank testing technology still lags the many recommendations put forward by the NAS committee and others.

### **Analytical Methods for Effectiveness**

Analytical means continues to be a major concern for effectiveness testing. It is very clear that only careful GC/MS techniques produce a true answer. There are few analytical methods that can be used outdoors or in field situations. Very early in the field testing program, fluorimeters were used. Studies then show that because the amount and distribution of PAHs, the target compound for fluorimeters, change with time during the course of a chemical dispersion event, a fluorimeter can never be truly 'calibrated' for a particular oil and dispersant combination. The invalid colorimetric method also continues to be used in a few cases for laboratory tests.

### **Toxicity of Dispersed Oil and Dispersants**

The results of dispersant toxicity testing are similar to that found in previous years, namely that dispersants vary in their toxicity to various species, however, dispersant toxicity is less than the toxicity of dispersed oil, by whatever tests.

Of the recent toxicity studies of dispersed oil, most researchers found that chemically-dispersed oil was more toxic than physically-dispersed oil. About half of these found that the cause for this was the increased PAHs (typically about 5 to 10 times) in the water column. Others noted the increased amount of total oil in the water column. Two researchers noted the damage to fish gills caused by the increased amount of droplets. A minority of researchers noted that chemically-dispersed oil was roughly equivalent to physically-dispersed oil.

The reasons for the change in findings in recent years might be attributed to better analytical techniques, both biological and chemical, as well as the use of newer tests. The increase in toxicity of chemically-dispersed oil can be attributed to: the increase (~ 5 times) in PAHs in the water column as a result of dispersant action, the large increase in number of droplets - conveying more oil into the water column, detected action of droplets on fish gills and increased partitioning of more toxic oil components from surface or sediment into the water column.

There are some studies departing from the traditional lethal aquatic toxicity assay and also some that focus on the longer-term effects of short term exposures. There certainly is a need for more of these types of studies. There is also a need to leave the traditional lethal assays and

use some of the newer tests for genotoxicity, endocrine disruption and others.

### **Biodegradation of Oil Treated by Dispersants**

Of the recent studies noted, about half of the researchers noted inhibition of oil biodegradation by dispersants and the other half found that biodegradation rates were about the same. No researcher in this time period noted, clearly found enhanced biodegradation as a result of dispersant use. The NAS committee notes in commenting on some of the old studies that overall one might note the experimental systems used to investigate biodegradation might be inappropriate to represent the environment, because they applied high mixing energy in an enclosed, nutrient sufficient environment and allowed sufficient time for microbial growth. Microbial growth on open-ocean slicks is likely to be nutrient limited and may be slow relative to other fate processes, many of which are resistant to biodegradation. It also noted that the most toxic components of the oil, the biodegradation of PAHs, has never been shown to be stimulated by dispersants (Committee, 2006). The study concludes that only PAH mineralization can be equated with toxicity reduction, stimulation of alkane biodegradation would not be meaningful in the overall toxicity of oil spills.

### **Spill-of-Opportunity Research**

Accurate and precise data from real spills would be most useful in making assessments and inputs for spill models. Essential data needs include: concentrations under the water column, effectiveness values, diffusion and transport values with currents and winds, separation between dissolved and droplet components, long-term data and detailed component analysis of the dispersed oil with time.

### **Monitoring Dispersant Applications**

Effectiveness monitoring at actual dispersant operations could provide very useful information for future assessment, modeling and basic understanding of chemical dispersion. Emphasis must be placed on obtaining accurate and precise data.

### **Dispersant Use in Recent Times**

Dispersant use in recent times is not well-documented or is in fact, decreasing. Scientific assessment of dispersant effectiveness at spill scenes is often not carried out.

### **Interaction with Sediment Particles**

The interaction of droplets, particularly chemically-dispersed droplets appears to be an important facet of oil fate. Although much more research is needed, it appears that high concentrations of sediment will have significant effect on dispersed oil droplets and the formation of stable OMAs (Oil-Mineral-Aggregates). OMAs appear to be stable over time and sink slowly and sediment on the bottom.

### **Stability of Dispersions and Resurfacing with Time**

Oil spill dispersions are not stable and dispersed oil will de-stabilize and rise to the surface. Half-lives of dispersions may be between 4 to 24 hours. More study on this is needed and this consideration requires to be incorporated into dispersant effectiveness studies.

### **Efficacy of Dispersants in Alaskan Waters**

The efficacy of dispersants in Alaskan waters remains an issue. There are contradictions in results from recent tank tests and from older field and tank tests. A recently-released report on effectiveness during the Exxon Valdez spill, shows that there was little to no effectiveness after dispersant application on this actual spill.

### **Weather and Application of Dispersants in Alaska**

Weather including temperature, winds and waves are an important consideration for oil spill dispersion. The weather 'window' for effective dispersant use may be small in Prince William Sound areas. There appears to be an interaction between salinity and temperature for oil spill dispersant effectiveness. Effectiveness appears to peak at about 15°C and about 25o/oo (parts-per-thousand). This may have an impact on effectiveness in areas such as Prince William Sound.

### **Fate of Dispersed Oil**

There are few, if any, thoughts on what the long-term fate of dispersed oil is. There are no studies that are relevant to Alaska field conditions.

### **Application Technology and Issues**

There was some work on application issues. Of particular significance was the development of single-point delivery systems. There are ASTM standards also now covering these. Some preliminary work was carried out on gelled dispersants.

### **Correlation of Oil Properties with Effectiveness**

Studies show good correlation with oil properties and dispersant effectiveness. The more specific the chemical property, the better the correlation.

### **Recommendations for Further Research**

The recommendations from the NAS committee are given as well as a workshop held on the same topic. The author of this report has given his own recommendations.



## **List of Acronyms**

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

BCF - Bioconcentration Factor - the ratio that a chemical accumulates in the body tissue versus that oxidized or passed through

CEWAF - Chemically-Enhanced Water Accommodated Fraction - The sum total of oil in a water sample including chemically and physically dispersed and soluble oil

CCO - cytochrome C oxidase - an enzyme that is measured and an indicator of stress in an organism

CDO - Chemically-Dispersed Oil

Corexit 9527 - Brand name of a dispersant from Exxon

Corexit 9500 - Brand name of a dispersant from Exxon

CROSERF - Chemical Response to Oil Spills: Ecological Research Forum - a group of scientists that set up new toxicity testing protocols in the late 1990's

CYP1A - Cytochrome P450 1A -Liver enzymes an enzyme that can be measured and indicators of stress in an organism

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

Enersperse - Brand name of a dispersant

EROD - ethoxyresorufin-O-deethylase - an enzyme that is a good indicator of hydrocarbon breakdown in an organism

EPA - U.S. Environmental Protection Agency

GC - Gas chromatography - a separation technique that is very common

GCMS - Gas chromatography Mass Spectrometry - the mass spectrometry is a powerful analytical technique

HLB - Hydrophilic-Lipophilic Balance - a theoretical measure of the oil-water solubility of surfactants

IFO - Intermediate Fuel Oil - A mixture of Bunker C and diesel used for ship propulsion - eg. IFO 180 and 380 refer to the viscosity of the oil at about 38°C.

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

LDH - lactate dehydrogenase - an enzyme that is measured and an indicator of stress in an organism

LOEC - Lowest Observable Effect Concentration - the lowest concentration that produces a noted effect

NAS - (U.S.) National Academy of Sciences

NOEL - No-Effect Level

OMA - Oil Mineral Aggregates

PAH - Polynuclear Aromatic Hydrocarbons

ΣPAH - the sum of PAHs in a given sample

PWSRCAC - Prince William Sound Regional Citizens' Advisory Council

SERVS - Ship Escort Response Vessel System - A division of Alyeska providing services in Prince William Sound

SPM - Suspended Particulate Matter

TPH - Total Petroleum Hydrocarbons - a measure of total hydrocarbons in a sample, usually by GC - FID

UV - Ultra Violet - the high energy part of the light spectrum

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

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## **1. Introduction**

### **1.1 Objectives**

The objectives of this review are to summarize the literature from the last report (2002) to the current date (2008) and to synthesize the literature to answer key questions relevant to the Prince William Sound Regional Citizens' Advisory Council (PWSRCAC).

### **1.2 Scope**

This review covers the literature from the last study sponsored by PWSRCAC and printed in 2002. As such it covers all known dispersant-related literature from that time period to August of 2008. While the study provides a summary of all the literature found, it focuses on literature that is more relevant to Prince William Sound.

### **1.3 Organization**

The report begins with a summary and then provides a detailed review of the literature. A review of the overall dispersant situation is presented in Section 2. In Section 3, the major issues of on effectiveness, toxicity and biodegradation, are discussed. In Section 4, other issues, particularly those relevant to PWSRCAC, are summarized as drawn from the literature review. Section 5 presents summaries of recommendations and this report's recommendations. Section 6 is a detailed review of the new literature, reference by reference. The literature is divided into peer-reviewed literature, reviewed conferences and 'grey' literature, that is literature which may not have undergone external review. Finally, Appendix A gives more details on methodology for this report and observations.

## 2 Overview of Dispersants

The use of dispersants still generates debate four decades after the Torrey Canyon incident. Some of the same issues predominate (Committee, 2006). The motivations for using dispersants are the same; reduce the possibility of shoreline impact; reduce the impact on birds and mammals; and promote the biodegradation of oil. The issues surrounding dispersants also remain the same; effectiveness, toxicity and long-term considerations. In summary, there are serious research gaps which have not been addressed over 40 years.

During the time for this review, the National Academy of Sciences released their study of the use of chemical dispersants in the United States. This report is particularly instructive and provides some very useful assessments of the situation. Their assessments and recommendations will be summarized in this report in the applicable sections.

### 2.1 Motivations for using dispersants

The prime motivation for using dispersants is to reduce the impact of oil on shoreline. To accomplish this, the dispersant application must be highly successful and effectiveness high. As some oil would come ashore, there is much discussion on what effectiveness is required to significantly reduce the shoreline impact (Committee, 2006). A major issue that remains is the actual effectiveness during spills so that these values can be used in estimates and models in the future.

The second motivation for using dispersants is to reduce the impact on birds and mammals on the water surface. As the NAS committee (2006) on dispersants notes, little or no research on this has been carried out anytime since the 1980's. They note on page 274 of their report, *“Of additional concern is the effect of dispersed oil and dispersants on the waterproof properties of feathers and their role as thermal insulators. One of the recommendations of the NRC (1989) report was that studies be undertaken to ‘assess the ability of fur and feathers to maintain the water-repellency critical for thermal insulation under dispersed oil exposure conditions comparable to those expected in the field’. This recommendation is reaffirmed because of the importance of this assumption in evaluating the environmental trade-offs associated with the use of oil dispersants in nearshore and estuarine systems because it has not been adequately addressed”* (Committee, 2006).

The third motivation for using dispersants is to ‘promote the biodegradation of oil in the water column’. The effect of dispersants on biodegradation is still a matter of dispute. There are a number of papers stating that dispersants do not promote biodegradation others indicate that dispersants suppress biodegradation. The most recent papers, however, confirm that promotion or suppression is a matter of the surfactant in the dispersant itself and the factors of environmental conditions. More details of recent findings will appear in the subsequent discussion. What is very clear at this time is that the surfactants in some of the current dispersant formulations can either suppress or have no effect on biodegradation. Further, there are issues about the biodegradability of the surfactants themselves and this fact can confound many tests of dispersed oil biodegradation. There are several unanswered questions, however. An important issue that never comes up is that it is known that oil-degrading bacteria, largely live on the water surface, where they would feed on similar natural hydrocarbons in the absence of spills. Would not putting oil in the water column then remove it from these bacteria? However, in the case of oil seeps or oil-contaminated sediments, there are microbial colonies associated at depth.

Another serious question is that of time scale. Biodegradation takes place over weeks, months and years. Dispersion half lives are 12 to 36 hours.

## **2.2 Dispersant Issues**

Effectiveness remains a major issue with oil spill dispersants. It is important to recognize that many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water. The most important of these is the composition of the oil, followed closely by sea energy and the amount of dispersant applied (Committee, 2006). It is equally important to recognize that **the only thing that counts in the end is effectiveness on real spills at sea**. More emphasis might be put on monitoring this so there is real information for assessment and modeling.

Effectiveness issues are confounded by the simple fact that small or large scale tests show highly different results depending on how they are constructed and operated. Detailed scientific examination of any of these shows major deficiencies. More emphasis is needed on looking at the real results from real spills.

Another major issue is that of the toxicity of dispersants and dispersed oil. The conventional wisdom is that physically-dispersed oil is as toxic as chemically-dispersed oil. Of course, a major point is that there is so much more of the chemically-dispersed oil in practice, given any sort of effectiveness (Committee, 2006). Will this increased amount of oil and oil components, be sufficient to cause short-term toxicity or long-term effects? Recent studies have also raised the issue of much-increased concentrations of PAHs (Polyaromatic Hydrocarbons) in the water column caused by the use of dispersants. These studies also show increased toxicity as a result of the PAHs. Long-term effects of chemically-dispersed oil are poorly-studied and relatively unknown at this point in time.

The last issue to be raised in this section is that of long-term effects. The long-term effects of chemically-dispersed oil have not been well studied and therefor remain largely as a topic for speculation. On a community level, there have been very few studies (Committee, 2006) such as the TROPICS study (Baca et al., 2005), however no molecular-level studies were undertaken on any of these studies.

## **3 Review of Major Dispersant Issues**

This section will explore the sub-topics of dispersant use, section by section. Information is drawn from the papers summarized in the back of this report, with emphasis on the peer reviewed literature.

### **3.1 Effectiveness**

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. Many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water. The most important of these is the composition of the oil, followed closely by sea energy and the amount of dispersant applied.

One of the major confusions that persist is the relationship of effectiveness to viscosity.



There is a certain belief that a ‘viscosity cutoff’ of effectiveness for dispersants exists. In fact, certain components of oil, such as resins, asphaltenes, and larger aromatics or waxes, are barely dispersible, if at all. Oils that are made up primarily of these components will disperse poorly when dispersants are applied. On the other hand, oils that contain mostly saturates, such as diesel fuel, will readily disperse both naturally and when dispersants are added. The additional amount of diesel dispersed when dispersants are used compared to the amount that would disperse naturally depends primarily on the amount of sea energy present. In general, less sea energy implies that a higher dose of dispersant is needed to yield the same degree of dispersion as when the sea energy is high. This should not be attributed to viscosity alone, but primarily to oil composition. Oils that typically contain a larger amount of resins, asphaltenes, and other heavier components are typically more viscous and less dispersible. Viscosity, however does not track composition very well and thus is only an indicator of dispersibility. A ‘viscosity cutoff’ does not exist.

While it is easier to measure the effectiveness of dispersants in the laboratory than in the field, laboratory tests may not be representative of actual conditions. Important factors that influence effectiveness, such as sea energy and salinity, may not be accurately reflected in laboratory tests. Results obtained from laboratory testing should therefore be viewed as representative only and not necessarily reflecting what would take place in actual conditions.

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 an oil slick on the surface. Any field measurement at this time is best viewed as an estimate.

The NAS committee on dispersants reviewed effectiveness testing (Committee, 2006). They noted that as the physical scale of the effectiveness increases, the cost and realism increase, but the degree to which factors that affect dispersion can be controlled and the ability to quantitatively measure effectiveness, decrease. It is noted that when modeling or prediction is carried out, that viscosity is an insufficient predictor of dispersion efficiency. The chemical composition of oil is important and several factors of composition have been shown to correlate well to dispersant effectiveness. Two other factors relating to dispersant effectiveness are the dispersant-to-oil ratio and the oil-to-water ratio, but the most important factor may be the energy applied, energy dissipation rate or mixing energy. In reviewing testing, the Committee notes that there are several important principles of experimental design which are often ignored including systematic errors which affect the outcome in one direction and random errors. Common systematic errors in dispersant effectiveness measurement included ignoring the evaporation of volatile compounds and incomplete recovery of floating oil. These two errors, as an example given in the NAS report, introduce a positive bias in the estimates of dispersant effectiveness.

The recommendations overall for effectiveness studies including: a focused set of studies should be developed to enable staff to predict effectiveness of dispersants for different oil types, environmental conditions over time; bench systems should be characterized for energy levels and particle sizes measured; the design of wave-tank studies should specifically test hypotheses regarding operational effectiveness; tank tests to test the recoverability of dispersed oil should be carried out; energy-dissipation tests should be carried out in wave-tanks; a mass balance should

be carried out in wave-tanks; and coalescence/ re-surfacing studies should be studied in flumes and wave-tanks; and more robust monitoring capabilities should be instituted to improve the quality of field data collected during dispersant applications (Committee, 2006).

### **3.1.1 Field Trials**

The U.S. National Academy of Sciences noted several items about field trials (Committee, 2006). The committee noted that field tests can provide opportunities to test and train on full scale equipment as well as to develop and test full scale monitoring equipment and to verify oil fate and transport models. Field tests are however, subject to high costs and legal issues may impede the conduction of these. A major limitation on field trials is the limited data set that can be obtained from one given trial. The experimental design of field trials is an issue and a primary objective should be to obtain an unbiased estimate of the variation that exists between two experimental slicks. Another major limitation on field trials is the inability to measure remaining oil slick thickness. Sorbent testing is not felt by NAS to be an accurate method. Measurement of oil in the water column is also fraught with difficulties, noting that the use of fluorometers only gives a relative measurement. The output of fluorometers also changes with time, aromatic composition, etc. Visual observation has been used, but a suggestion to improve this is to use 'blind' observers who are not aware of the particular treatment applied. Visual observation is subject to many variables including position of the sun, cloud cover and viewing angle. The committee notes that results from field trials are generally lower than that obtained in the laboratory suggesting that the energy regimes in the laboratory are higher than encountered in those field trials. Mass balances should also be attempted on field trials. In conclusion, the complexities and costs of carrying out meaningful field trials suggest that more effort be placed on improving bench-scale and mesocosm research projects. As a recommendation, it is stated that future field-scale work should be based on systematic and coordinated bench-scale and wave-tank testing as recommended.

Many field trials have been conducted in the past to assess the effectiveness of dispersants. Several papers have assessed the techniques used to measure effectiveness in these tests (Fingas and Ka'aihue, 2004). There is no general consensus that effectiveness and other parameters can actually be measured in the field using some of the current methodologies.

The effectiveness determined during these trials varies significantly. Recent results, which may be more reliable, claim that dispersants removed about 10 to 40% of the oil to the sub-surface (Committee, 2006). The validity of much older test results is even more questionable because of both the analytical methodology, which is now known to be incorrect, and data treatment methods (Fingas and Ka'aihue, 2004). It is interesting that the percentage values assigned average 16%, both in the older and more recent field trials (Fingas, 2002).

All tests relied heavily on developing a mass balance between oil in the water column and that left on the surface. In early tests, samples from under the oil plume were analysed in a laboratory using colorimetric methods, which are notoriously inaccurate and are no longer used. Fluorometry has recently been used, but this method is also 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. There is further discussion on analytical techniques in a later section of this report.

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 away from the slick in a separate trajectory. 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. Since the colorimetric techniques used at the time always yielded some value, the effectiveness values were significantly increased. When effectiveness values from past tests were recalculated using only the area where the plume was known to be, those values decreased by factors as much as 2 to 5 (Fingas, 2002).

In summary, testing in the field is difficult because effectiveness values depend on establishing a mass balance between oil in the water column and on the surface. Because this mass balance is difficult to achieve, results are questionable in many cases.

### **3.1.2 Laboratory Tests**

Many different types of procedures and apparatus for testing dispersants are described in the literature. Fifty different tests or procedures are described in one paper (Fingas, 2002). Only a handful of these are commonly used, however, including the Labofina, Warren Springs or rotating flask test, the swirling flask test, and the baffled flask test.

Several investigators have reported results of apparatus comparison tests conducted in early years. In the 11 papers reviewed, all authors concluded that the results of the different tests do not correlate well, but some conclude that some of the rankings are preserved in different tests. Generally, the more different types of oil tested, the less the results correlate. It has been shown that laboratory tests can be designed to give a comparable value of oil dispersion if the parameters of turbulent energy, oil-to-water ratio, and settling time are set at similar values - but most importantly if correct analytical procedures are applied (Fingas, 2002).

In the literature, different protocols are sometimes described for the same apparatus. The protocol used can sometimes change the data more than the actual physical test.

Fingas (2004, 2005a, 2005b) calculated or estimated energy and work in several laboratory vessels and compared to estimates of energy/work at sea. Some measurements completed by PIV and anemometry were compared to these calculated values. The initial measurements and estimates indicate that the energy in several laboratory vessels is similar and that it may be equivalent to those encountered at sea under moderate wind and wave conditions. Two techniques have been initiated to measure energy. The measurement technique chosen to do this is Particle Image Velocimetry or PIV. In this method, seed particles - which could be oil droplets, are put into the fluid and the fluid is illuminated with a laser. The movement of a particle in a given cell is measured as a function of time. This can occur as fast as 30 to 100 Hz, depending on the apparatus. Turbulent energy can be calculated at each point in the image frame. The other method used is hot wire anemometry. This method can yield data similar to PIV, however requires the intrusion of a probe into the area. The methods are compared in several laboratory vessels under several energy conditions.

There has been a lot of recent work on the new EPA test entitled the Baffled Flask (Chandrasekar et al., 2005; 2006; Kaku et al., 2005, 2006; Sorial, I, II, 2004; Srinivasan, 2007). This apparatus has been studied thoroughly including energy studies, variation with temperature, salinity and operational parameters. This test is a high-energy test and uses an old colorimetric analytical method.

In an inter-laboratory evaluation of dispersant effectiveness tests, there was some agreement between test results on fresh oils, but very poor agreement between results of tests on oils that were more weathered or had any amount of water content. Some of these laboratory data were compared to the field data by Lunel and coworkers and the results are shown in Table 1 (from Fingas, 2002; repeated in Committee, 2006). 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 thought in previous years. Some workers continue to scale up the energy of laboratory tests while these data in Table 1 and other data clearly show that the two lower energy tests, the swirling flask and Warren Springs test come closest to the best field measurements to date. Although they are considered low-energy tests, they are still well-above the field test results. This indicates that the low-energy tests might even be still too high in energy.

<b>Table 1 Comparison of Laboratory and Field Effectiveness Results</b>								
Oil type	Dispersant	Field Test	Effectiveness Results in Percent					Exdet
			SF	SF	IFP	WSL	WSL	
			GC	CA		Lab 1	Lab 2	
Medium fuel oil	Corexit 9527	26	54	50	91	42	42	67
Medium fuel oil	Slickgone NS	17	49	46	94	29	23	50
Medium fuel oil	LA 1834/Sur	4	2	2	50	16	11	38
Forties crude	Slickgone NS	16	47	65	95	28	25	60
Forties crude	LA 1834/Sur	5	2	2	61	15	12	53
<b>Correlation with field test (<math>R^2</math>)</b>			0.89	0.7	0.54	0.87	0.94	0.41
<b>Ratio Lab test/field test</b>			0.4	0.35	0.19	0.56	0.62	0.27
<i>Legend SF = Swirling Flask, GC= analysis by Gas Chromatography, CA= Colorimetric Analysis,</i>								
<i>IFP = French Institute for Petroleum test, WSL = Warren Springs Laboratory Test</i>								

The National Academy noted several items about laboratory tests (Committee, 2006). Bench scale testing is widely used to evaluate the performance of dispersants and the physical and chemical mechanisms of oil dispersion. A major disadvantage is, of course, that it is difficult to scale the results of these tests to predict performance in the field. Several factors that are difficult to extrapolate include energy regimes, dilution due to horizontal and vertical advection and turbulent diffusion. Bench scale tests are very useful for determining the effectiveness of various dispersant-oil combinations, salinity, temperature effects, effects of oil composition and effects of oil weathering. Recommendations are that energy dissipation rates should be determined over a range of operation conditions, that dispersant effectiveness be measured over a range of energy regimes and that droplet size be measured.

### 3.1.3 Tank Tests

Tank tests continued at a high level. The U.S. National Academy focussed much attention on tank testing (Committee, 2006). They note that the physical characteristics of wave tanks

imply that the encounter probability of the dispersant with the oil slick will be higher than can be achieved during a real spill response. Thus, wave-tank tests provide upper limits on operational effectiveness. There is concern that wave-tank tests may also not count for the skinning of oil that often occurs with weathering. Another concern is that the dispersant application system should simulate the droplet-size distributions and impact velocities in real application systems. The wave energies used in tanks should be scalable to actual sea states. It is also noted that coalescence and resurfacing of dispersed oil droplets occur and wave-tank experiments should include investigation of these phenomena. A number of wave tanks are portrayed. In summary, it is noted that the advantage of wave tanks is to investigate operational effectiveness components and observe diffusion of droplets more like at sea. The dispersant droplet size generation in tanks may be an important factor. The committee feels that the measurement of effectiveness should also include the measurement of dispersed oil droplet size. The measurement of effectiveness should include the determination of mass balances (Goodman, 2005). It is noted that in tanks where this is attempted, mass balances typically vary from 50 to 75%. It is recommended that mass balance should be attempted in all wave-tank studies of dispersant effectiveness.

Mass balance remains a large issue. Several testing groups were able to establish mass balances in their tanks to enable more accurate assessments of dispersant effectiveness. Bonner et al. (2003; Page et al., 2002) developed a materials balance approach in conducting petroleum experiments at the SERF facility. The first attempt at a materials balance was during a 1998 study on the fate/effects of dispersant use on crude oil. Both water column and beach sediment samples were collected. For the materials balance, the defined environmental compartments for oil accumulation were sediments, water column, and the water surface, while the discharge from the tanks was presumed to be the primary sink. The factors that required development included a need to quantify oil adhesion to the tank surfaces. This was resolved by adhering strips of the polymer tank lining to the tank sides that could be later removed and extracted for oil. A water-surface oil slick quantification protocol was developed, using solid-phase extraction disks.

EPA and the Canadian Department of Fisheries constructed a new test tank at Bedford Nova Scotia. Extensive calibration, wave and energy measurement were carried out at this facility (Li et al., 2007, 2008).

OHMSETT continued work on dispersants (Belore, 2003, Belore et al., 2008, SLR, 2003, 2004, 2005, 2006, 2007; Trudel and Belore, 2005).

The present author and co-workers prepared extensive studies on tank testing (Fingas, 2003, Fingas and Ka'ahue, 2004; Fingas and Decola, 2006). The following are 17 critical factors that need to be considered and included in any test for measuring the effectiveness of dispersants in a tank in order for that test to be valid.

1. Mass balance - Mass balance should be calculated and maintained in the best way possible. Because of the difficulty in accounting for all the oil, dispersant effectiveness should not be taken as the oil unaccounted for. In historical experiments, the oil unaccounted for ranged from - 20% (over-accounted) to over 80%. In one set of experiments, Brown et al. (1987) showed that lack of mass balance would exaggerate apparent effectiveness on average by a factor of 4 times.
2. Proper controls - Dispersant effectiveness must always be directly related to an identical experiment, preferably conducted at the same time under identical conditions as the test with dispersants. It should be noted that dispersants cause other changes in oil behaviour and a simple comparison to an untreated control may not be valid.

3. Analytical method - There are few analytical methods that can be directly applied outside the laboratory. Fluorometry is one of these, but must be calibrated using standard sample analysis taken at the same time in the field. Furthermore, this calibration must be carried out using certified methods by a certified chemist in a certified laboratory. But .. as the PAHs that fluorometry measures, this value changes over time, space and conditions and thus is only an indicator – not a true measure.
4. Differential plume movement - The geometry and movement of the dispersed oil plume are different from the surface slick and the surface slick cannot be used to guide sampling of the dispersed oil plume.
5. Time lag and length of time plume followed - There is a time lag of 15 to 90 minutes before maximum dispersion takes place. Furthermore, because of resurfacing of oil, the plume loses oil over a 2-day period. These dynamics must be considered in designing experiments.
6. Mathematics of calculation and integration - It is shown that several errors can be made in integration. Averages should not be used over wide areas and only the specific dispersant plume should be integrated.
7. Lower and upper limits of analytical methods - The analytical methods used must have the dynamic range to cover background levels to the peak dispersant plume value, generally from 0.1 to 100 ppm.
8. Thickness measurement - There are no valid and reliable thickness measurement techniques for surface slicks. Thus any value is an estimation and may easily be in error by an order-of-magnitude. This makes it difficult to perform mass balance on the basis of surface measurements. Thin slick quantities have been estimated using specially developed techniques (Bonner et al., 2003).
9. Behaviour of oil with surfactant content - Oil with surfactant content behaves differently than oil without. The critical containment velocity is much less. Its adhesion to sorbent-surface skimming devices is poor. Use of containment near critical velocity simply results in the release of oil after dispersant treatment, not dispersion.
10. Surfactant stripping - Surfactants partition out of the oil droplets over time, destabilising the dispersed droplets and resulting in oil resurfacing. This occurs slowly and could occur over a wide area. Furthermore, slicks resulting from these phenomena are probably not thick enough to be observed.
11. Recovering surface oil - Recovering surface oil to calculate mass balance has a variety of problems including the loss of sheen (not an insignificant amount of oil in a large tank) and invisible sheen as well as evaporation loss. The surfactants cause poor adhesion and poor recovery when using spray or water discharge systems.
12. Background levels of hydrocarbons - The background levels of hydrocarbons must be used to correct measurements. The levels may vary widely and should be treated with the same caution as actual data.
13. Fluorescence of dispersant - The dispersant itself yields a fluorescent value, sometimes as much as 5 ppm- equivalent. This is largely due to light scattering in the fluorometer and should be corrected for.
14. Herding - Herding of oil occurs when larger droplets break through the slick and the surface pressure of the dispersant pushes oil aside. Herding is a major interference in conducting dispersant field trials and should be considered in tank tests.

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

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

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

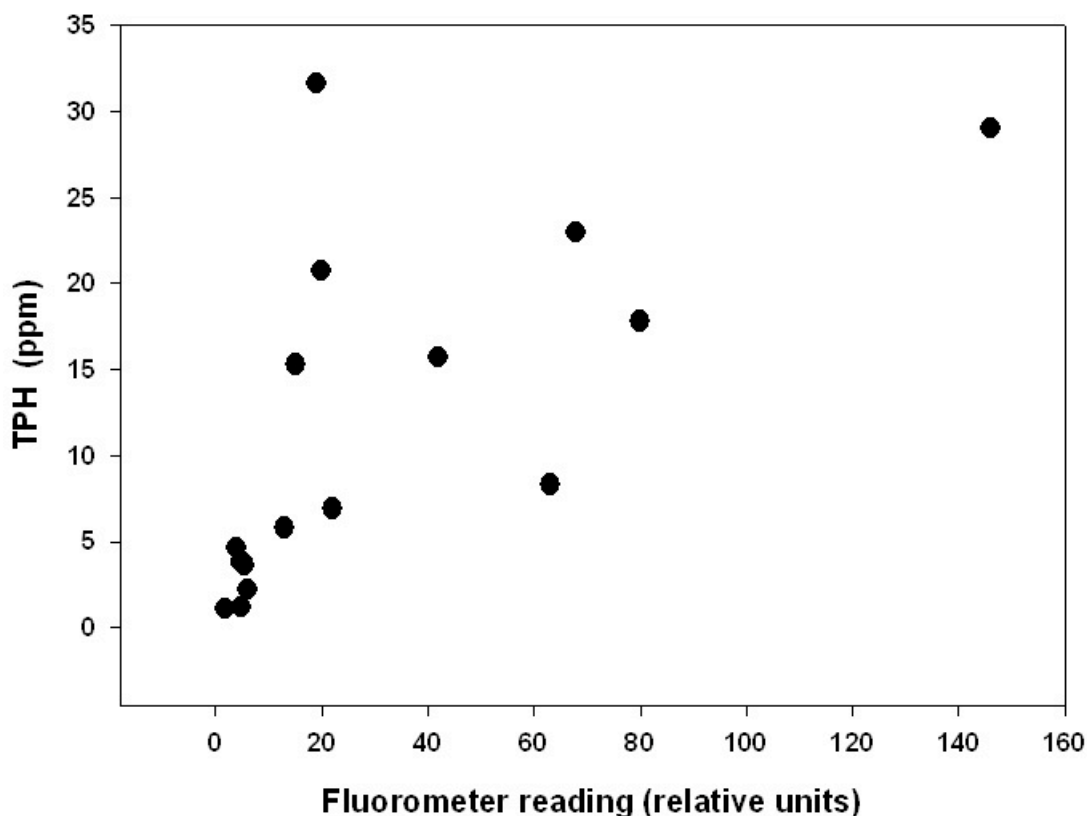
Each of these factors is important to the appropriate outcome of the dispersant tank experiment. Important factors are the ability to determine a mass balance, the use of proper controls and analytical methods.

### **3.1.4 Analytical Means**

Analytical means in any test system continues to be a major concern. It should be made very clear that only careful GC/MS techniques produce a true answer (Lambert, 2003). There are few analytical methods that can be used outdoors or in field situations. Very early in the field testing program, fluorimeters, particularly Turner fluorimeters, were used. Studies then showed that because the amount and distribution of PAHs, the target compound for fluorimeters, change with time during the course of a chemical dispersion event, a fluorimeter can never be truly 'calibrated' for a particular oil and dispersant combination (Fingas and Ka'ahue, 2004; Fingas and Decola, 2006). A fluorimeter uses UV or near UV to activate aromatic species in the oil. The UV activation energy is more applicable 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. A fluorimeter reading will always remain a relative value and even with careful calibration can only give indications that are as much as order-of-magnitude from the true value. Efforts continue on fluorescent measures (Bugden et al., 2008), however there needs to be more recognition that this method will always be relative and highly prone to error.

Even with good calibration and taking samples directly from the output of a fluorimeter, there are significant differences because the target compound of the PAHs have different distributions and concentrations with time, conditions and weathering of the oil. Figure 1, below shows the lack of relation between the TPH measured by GC-FID and the reading of the fluorometer. Samples for analysis were taken directly from the output of the fluorometer and readings recorded for comparison. Figure 1 shows that the correlation between readings is poor.

Some of the earlier trials used grab samples which were subsequently taken for analysis by UV or IR absorption. 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 bacterial growth and hydrocarbon loss. There are standard procedures available, but in early trials these were not applied.



**Figure 1      The Lack of Correlation between Fluorometer Reading and Actual GC-FID Measured TPH during Actual Tank Trials. The Samples for TPH Analysis Were Drawn from the Fluorometer Output.**

Another analytical issue in the field of effectiveness measurement is the use of colorimetric measures. The basic science of the issue is this: to be a valid colorimetric measurement, the analyte must have a chromophore or color-absorbing center and the system must obey the Beer-Lambert law (linear absorption over broad range of concentrations)(Fingas, 2002). Oil does neither of these two things. Oil is a mixture of dozens to hundreds of compounds, none with a chromophore, visible light absorbing center. Further, what occurs in an oil-in-solvent system is simply light blockage. In analytical chemistry, colorimetry is never used, even when valid, because of the many problems, interferences and inaccuracies. Only gas chromatography and detection by mass spectrometry or flame ionization are considered valid techniques.

### 3.2 Toxicity

The second important issue when discussing dispersants is toxicity, both of the dispersant itself and of the dispersed oil droplets. Toxicity became an important issue in the late 1960s and early 1970s when application of toxic products resulted in substantial loss of sea life. For example, the use of dispersants during the *Torrey Canyon* episode in Great Britain in 1968 caused massive damage to intertidal and sub-tidal life (Fingas, 2000). Since that time, dispersants have



been formulated with lesser aquatic toxicity. Although, the issue may not be the toxicity of the dispersant itself but the large increase in the oil droplets in the water and the large increase in PAHs in the water column as a result of dispersant use.

A standard toxicity test is to measure the acute toxicity to a standard species such as the rainbow trout. The  $LC_{50}$  of a substance is the 'Lethal Concentration to 50% of a test population', usually given in mg/L, which is approximately equivalent to parts per million. The specification is also given with a time period, which is often 96 hours for larger test organisms such as fish. The smaller the  $LC_{50}$  number, the more toxic the product. The toxicity of dispersants used in the early 1970s ranged from about 5 to 50 mg/L measured as an  $LC_{50}$  to the rainbow trout over 96 hours. Dispersants available today vary from 200 to 500 mg/L ( $LC_{50}$ ) in toxicity and contain a mixture of surfactants and a less toxic solvent.

The oil itself is may be more toxic to most species than the dispersants, with the  $LC_{50}$  of diesel and light crude oil typically ranging from 20 to 50 mg/L for either chemically or naturally dispersed oil. The natural or chemical dispersion of oil in shallow waters can result in a mixture that is toxic to sea life. For example, a spill in 1996 from the *North Cape* in a shallow bay on the U.S. Atlantic coast caused massive loss of benthic life without the use of dispersants. Another significant factor in terms of the impact of this spill was the closeness to shore which caused a high concentration of hydrocarbons in the water.

The U.S. National Academy of Sciences report on dispersants had many thoughts on toxicity (Committee, 2006). The reports notes several times that there is insufficient understanding of the fate of dispersed oil in aquatic systems, particularly interaction with sediment particles and subsequent effects on the biotic components. The relative important of different routes of exposure, that is, the uptake and associated toxicity of oil as dissolved components compared to oil droplets and also as mineral particle-associated droplets is poorly understood. Many exposure models and studies do not consider these differences either. The new trends in ecotoxicology, that is population and community-level approaches are gaining wider acceptance in general, and hopefully will be more accepted in the oil spill community in the future.

Testing procedures are also summarized by the committee, noting that the standard short-term lethal toxicity test data are abundant, but may not be sufficient to assess the potential risk of dispersed oil (Committee, 2006). These short-term tests are also inadequate to assess potential delayed effects due to oil metabolism, bioaccumulation and photoenhanced toxicity. Some protocols for producing dispersed and chemically-dispersed oil are reviewed. Toxicity testing using common procedures varies the dose of the solution compared to an alternate procedure of diluting test procedures. Advantages of both common procedures are discussed. It is also noted that better exposure quantification is required and testing should move away from 'nominal doses' or simply calculating on the basis of added material. The difference in solubility of the materials can result in orders-of-magnitude errors if using nominal dosage methods. Better testing methods have used TPH or total petroleum hydrocarbons. Advanced methods use and will use quantification by classes such as alkanes, BTEX, and PAHs. Many studies have quantified as many as 50 PAHs in the toxicants.

The 2006 committee noted that the 1989 dispersant report concluded that the acute lethal toxicity of chemically-dispersed oil is primarily associated with the dispersed oil and dissolved oil constituents. However, several studies are noted in which this conclusion is not valid and the conclusion should be reexamined. Sensitivity to dispersants and dispersants varies significantly

by species and life stage. Embryonic and larval stages are more sensitive than adults to both dispersants and dispersed oil. Excellent tables of acute toxicity results are given in this chapter in which these conclusions are shown. In addition to acute toxicity, dispersant may have more subtle effects that influence health of organisms. As an example, dispersants have been reported to affect the uptake of oil constituents. It should be noted, that there is a dearth of longer-term studies on the toxicity of dispersants themselves.

The toxicity of dispersed oil has been examined in a number of studies as summarized by the NAS (Committee, 2006). As oil consists of many classes of compounds and hundreds of individual compounds, aquatic organisms are potentially exposed to many toxicants with different modes of action and via different exposure routes. The actual toxicity of dispersed oil in the environment depends on many factors: effectiveness of the dispersion, mixing energy, oil type, weathering of the oil, dispersant type, temperature, salinity, exposure duration and light penetration into the water column. In actual practice, some weathering (several hours) would occur after the spill resulting in the loss of many volatiles and enriching the oil in PAHs. PAH toxicity is primal, however several studies have noted that other components in the oil account for much of the toxicity as well. For some organisms, dispersed droplets are also an important route of exposure, either through droplet/gill interactions or through ingestion. Studies show that some organisms accumulate PAHs differently via particulate or dissolved routes. Organisms may also be exposed to oil by contamination of their food. Many oil constituents, such as the monoaromatics and PAHs, are narcotics, that is substances which causes a state of arrested activity of protoplasmic structures.

Several laboratory studies as summarized by NAS, indicate that PAH toxicity increases (from about 12 to about 50,000 times) in exposures conducted with UV light present as it would be in nature in shallow waters (Committee, 2006). Photo-enhanced toxicity consists of two mechanisms, but the most important one is photosensitization. This occurs when a PAH absorbs energy from the light and then transfers this to dissolved oxygen. This results in enhanced toxicity to many organisms.

The literature reviewed up to the committee's period of writing, indicated that there was no consensus in the relative toxicities of chemically and physically dispersed oil (Committee, 2006). Many studies found that the PAH concentration is much higher in chemically-dispersed oil than for physically-dispersed oil. Several researchers have recently noted higher toxicities of chemically-dispersed oil. Some studies have also noted that the PAH bioaccumulation kinetics are increased in chemical dispersions. Depuration rates were found to either increase or decrease, depending on the organism. A useful table of chemically-dispersed and physically-dispersed toxicity is given in the report.

The NAS comment on freshwater as well (Committee, 2006). It was noted that the amount of literature related to effects on freshwater organisms is low. This is attributed to the fact that most common U.S. dispersants have low freshwater efficacy and that the use of dispersants in freshwater is unlikely since most water bodies provide a source of drinking water.

Little is known about the effects of dispersant or dispersed oil on wildlife. The report speculates, that while chemical dispersants may lower the amount of oil to which a bird or aquatic mammal is exposed to, potentially there may be a loss of insulation through reduction of surface tension at the feather/fur-water interface. Since this is a very important factor, more research on this aspect is needed.

Toxicity issues related to microbes have not been well studied and may be confounded by a number of side phenomena, some of which are described in the report (Committee, 2006).

Coral reefs are noted as being very sensitive to oil or dispersants because the tissue over the skeleton is very thin and because oil droplets adhere to the surface of the organism. Data are currently limited and further studies are recommended.

The committee's recommendations for further studies include: quantifying the weathering and fate of chemically-dispersed oil compared to undispersed oil; obtain data on dissolve-phase PAH and particulate/oil-droplet phase PAH concentrations in test tanks or ideally, at spills-of-opportunity; assess the ability of fur and feathers to maintain water-repellency under dispersed oil exposure conditions; and conduct a series of focused toxicity studies to provide data on photo-enhanced toxicity, estimate the contributions of dissolved and particulate oil phases to toxicity and expand toxicity tests to include delayed effects (Committee, 2006).

Of particular concern is the actual toxicity of the dispersed oil - compared to physically-dispersed oil. There are several studies on this currently and peer-reviewed examples of this are noted below:

A study of benzo(a)pyrene type (BaP) and naphthalene-type metabolite elimination in Australian bass after exposure to Bass Strait crude oil and chemically-dispersed crude oil was carried out by Cohen et al. (2003). Chemically dispersing the crude oil resulted in five times higher concentrations of TPH in the water column, compared to the water soluble fractions alone. There was only a slightly higher amount of the PAH biliary metabolic concentrations after four days in the dispersed samples. This difference disappeared after 12 days depuration and the oil-only had very slightly higher levels. This slight difference was attributed to the fact that the dispersed crude increased metabolic activity and causes a higher degree of sub-lethal stress. Cohen et al. (2005) again studied Australian bass exposure to the water-accommodated fractions of Bass Strait crude oil or dispersed crude oil to assess sublethal effects of oil spill remediation techniques on fish. Fish were exposed to these treatments for 16 days either through the water column or by way of a pre-exposed diet of an amphipod. Fish gills, liver, and white muscle were sampled and cytochrome C oxidase and lactate dehydrogenase activities quantified. In all treatments fish exposed by way of the water column, aerobic activity increased in the gills, whereas a decrease of this enzymic activity was observed in the liver and white muscle. Exposures by way of the food pathway indicated similar trends. Anaerobic activity increased in the gills, liver, and white muscle after waterborne exposures. Stimulation in anaerobic activity also occurred in the liver and white muscle of fish after exposure to contaminated food. Oxidase activity in the gills was the most sensitive biomarker when monitoring waterborne exposures to petroleum hydrocarbons. In the gills, the dispersed oil treatment resulted in the most pronounced biological response, suggesting that in the short term the use of dispersants on an oil slick might cause the most perturbations to fish metabolism.

Couillard et al. (2005) exposed newly hatched mummichog were exposed in a 96-h static renewal assay to water-accommodated fractions of dispersed crude oil (DWAF)(Dispersed Water Accommodated Fraction) or crude oil (WAF) (Water Accommodated Fraction) to evaluate if dispersant-induced changes in aqueous concentrations of polycyclic aromatic hydrocarbons (PAH) affected larval survival, body length, or ethoxyresorufin-O-deethylase (EROD) activity. Weathered Mesa light crude oil and filtered seawater with or without the addition of Corexit 9500 were used to prepare DWAF and WAF, respectively. At 0.2 g/L, the addition of dispersant caused

a two- and fivefold increase in the concentrations of total PAH and high-molecular-weight PAH (HMWPAH) with three or more benzene rings. Highest mortality rates (89%) were observed in larvae exposed to DWAF. A reduction in body length was correlated with increased levels of  $\Sigma$ PAH and not with HMWPAH. The EROD activity increased linearly with HMWPAH and not with  $\Sigma$ PAH. Chemical dispersion increased both the  $\Sigma$ PAH concentrations and the proportion of HMWPAH in WAF. Dispersed HMWPAH were bioavailable, as indicated by a significantly increased EROD activity in exposed mummichog larvae.

Fuller et al. (2004) evaluated the relative toxicity of oil, dispersant or both substances, both on a continuous and a declining concentration over time. Two fish species and a shrimp, were used. Microbial toxicity was evaluated using Microtox. The results suggested that the oil and dispersant mixtures were about the same or less toxicity than the oil mixtures alone. The continuous exposures yielded more toxicity than the declining exposure conditions. Unweathered oil fractions were more toxic than the weathered fractions of the same oil. Toxicity appeared to be largely as a result of the soluble oil components.

Georgiades et al. (2003) examined exposure to oil-derived products and results from countermeasures on the behaviour and physiology of the Australian 11-armed asteroid. Asteroids were exposed to dilutions of water-accommodated fraction (WAF) of Bass Strait stabilised crude oil, dispersed oil or burnt oil for 4 days and prey localization behaviour was examined immediately after exposure, and following 2, 7, and 14 days depuration in clean seawater. The prey-localization behaviour of asteroids exposed to WAF and dispersed oil was significantly affected though recovery was apparent following 7 and 14 days depuration, respectively. Behavioral impacts were correlated with the total petroleum hydrocarbon concentrations (C6–C36) in each exposure solution, WAF (1.8 mg /L), dispersed oil (3.5 mg/L) and burnt oil (1.14 mg/L), respectively. The total microsomal cytochrome P450 content was significantly lower in asteroids exposed to dispersed oil than in any other asteroids, whilst asteroid alkaline phosphatase activity was not significantly affected.

Khan and Payne (2005) studied on the influence of dispersant, Corexit 9527, and dispersed oil on mature members of Capelin, Atlantic Cod, Longhorn Sculpin and Cunner. Exposure was for 96 hours. The acute studies showed that mortality was greater in both cod and sculpin exposed to dispersant-WAF mixtures than for any other group. Both the dispersant and the WAF also caused mortality in the cod, but not to the cunner. Examination of gill lesions in the same species showed that epithelial separation and rupture of the secondary lamellae of the gills were observed in fish following exposure to any of the 3 challenges. The percentage of gill lesions was generally greater with the dispersed oil. The authors note that the increase in gill lesions was probably as a result of dispersant-enhanced toxicity.

Koyama and Kakuno (2004) studied the toxicity of three dispersants and heavy fuel oil to a marine fish, red sea bream. The mean lethal oil concentration of the water-accommodated oil fraction was 325 mg/L. Mixtures of oil and dispersant were more toxic than dispersant or oil alone. Use of a dispersant-to-oil percentage of 20%, which is recommended by the manufacturer because of its efficiency in oil emulsification and dispersion, yielded higher 24-h oil concentrations and resulted in a higher mortality rate than did the use of higher percentages of dispersant.

Liu et al. (2006) conducted a field investigation on a Louisiana Spartina shoreline to evaluate the toxic effects of crude oil (Alaska North Slope crude oil, ANS) and dispersed oil (ANS +

dispersant Corexit 9500) on three aquatic species indigenous to the Gulf of Mexico: Gulf killifish, Eastern oyster, and white shrimp. Results indicated that total hydrocarbon concentration value in oiled treatments decreased rapidly in 3 h and were below 1 ppm at 24 h after initial treatment. Corexit 9500 facilitated more ANS fractions to dissolve and disperse into the water column. The shrimp showed short-term sensitivity to the ANS and ANSC + 9500 at 30 ppm. However, most test organisms of each species survived well after 24 h exposure to the treatments. Laboratory tests conducted concurrent with the field investigation indicated that concentrations of crude oil higher than 30 ppm were required for any significant toxic effect on the juvenile organisms tested.

Long and Holdway (2002) investigated the effects of acute exposure to crude and dispersed crude oil and a reference toxicant, on recently hatched octopus. Water-accommodated fraction (WAF) of Bass Strait crude oil was prepared using a ratio of one part crude oil to nine parts filtered seawater and mixing for 23 h. Dispersed-WAF was prepared using a ratio of one part Corexit 9527 to 50 parts crude oil and an oil to water ratio of one to nine and mixing for 23 h. The 48 h LC<sub>50</sub> values were similar for WAF, dispersed-WAF and the reference toxicant.

Yamada et al. (2003) studied the fate of PAHs with and without dispersants in 500 L tanks with seawater. Samples of water and particles were analyzed for 38 PAHs. Low molecular weight PAHs (with less than 3 rings) disappeared rapidly, generally within 2 days. High molecular weight PAHs (with more than 4 rings) remained in the water column for longer times, up to 9 days. Significant portions (10 to 94%) of the high molecular weight PAHs settled to the bottom and were caught in the sediment trap. The addition of chemical dispersant accelerated the biodegradation of PAHs but amplified the amount of PAHs found in the water column. The water column enrichment factor caused by dispersants was up to 6 times. The increased PAHs appeared to overwhelm the biodegradation and thus higher concentrations were observed in the dispersant-treated tanks throughout the experiment. The dispersant appeared to reduce the amount of heavy PAHs sedimented and put these into the water column.

Ramachandran et al. (2004) conducted an experiment to measure whether oil dispersion increases or decreases the exposure of aquatic species to the toxic components of oil. To evaluate whether fish would be exposed to more polycyclic aromatic hydrocarbon (PAH) in dispersed oil relative to equivalent amounts of the water-accommodated fraction (WAF), measurements were made of CYP1A induction in trout exposed to the dispersant, Corexit 9500, WAFs, and the chemically enhanced WAF (CEWAF) of three crude oils. The crude oils comprised the higher viscosity Mesa and Terra Nova and the less viscous Scotian Light. Total petroleum hydrocarbon and PAH concentrations in the test media were determined to relate the observed CYP1A induction in trout to dissolved fractions of the crude oil. CYP1A induction was 6- to 1100-fold higher in CEWAF treatments than in WAF treatments, with Terra Nova having the greatest increase, followed by Mesa and Scotian Light. Mesa had the highest induction potential with the lowest EC<sub>50</sub> values for both WAF and CEWAF. The dispersant Corexit was not an inducer and it did not appear to affect the permeability of the gill surface to known inducers such as  $\beta$ -naphthoflavone. These experiments suggest that the use of oil dispersants will increase the exposure of fish to hydrocarbons in crude oil.

Mielbrecht et al. (2005) investigated the influence of a chemical dispersant on the uptake, biotransformation, and depuration of a model hydrocarbon, [<sup>14</sup>C]-phenanthrene ([<sup>14</sup>C]PHN), by larval topmelt. Exposure was via aqueous-only or combined dietary and aqueous routes from a water-accommodated fraction (WAF) of Prudhoe Bay Crude Oil or a WAF of Corexit 9527-

dispersed PBCO (DO). Trophic transfer was measured by incorporating into exposure media both a rotifer, as food for the fish and a phytoplankton, as food for the rotifers. Short-term (<4 h) bioconcentration of PHN was significantly decreased in topsmelt when oil was treated with dispersant, but differences diminished after 12 hours. When trophic transfer was incorporated, PHN accumulation was initially delayed but after 12 h attained similar levels. Dispersant use also significantly decreased the proportion of biotransformed PHN (as 9-phenanthrylsulfate) produced by topsmelt. A chemical dispersant use in oil spill response may reduce short-term uptake but not long-term accumulation of hydrocarbons such as PHN in pelagic fish.

Otitoloju (2005) evaluated the toxicities of a Nigerian crude oil, a dispersant, Biosolve, and their mixtures, based on ratios 9:1, 6:1 and 4:1 (v/v), against the juvenile stage of a prawn in laboratory bioassays. On the basis of the derived toxicity indices, crude oil with 96-h  $LC_{50}$  value of 0.28 ml/L was found to be about six times more toxic than the dispersant (96-h  $LC_{50}$  1.9 ml/L) when acting alone against the prawn. Toxicity evaluations of the mixtures of crude oil and dispersant revealed that effects of the crude oil/dispersant mixtures varied, depending largely upon the proportion of addition of the mixture components. The interactions between mixture of crude oil and dispersant at the test ratios of 9:1 and 4:1 were found to conform with the model of synergism, while the interactions between the mixture prepared based on ratio 6:1 conformed with the model of antagonism, based on the concentration addition model. Furthermore, the mixtures prepared based on ratios 9:1 and 6:1 were found to be less toxic than crude oil when acting singly against the prawn while the mixture prepared based on ratio 4:1 was found to have similar toxicity with crude oil when acting singly, based on the derived synergistic ratio values.

Perkins et al. (2005) tested the toxicity of oil and dispersed oil to a cold-water species, Tanner crab larvae, and compares the result to two standard warm-water test species, the saltwater mysid and fish larvae. The method of reporting the exposure dose: loading rate, volatile organic analytes (VOA, C6–C9), total petroleum hydrocarbons (TPH C10–C36), or their summation, total hydrocarbon concentrations (THC C6–C36) would result in different conclusions. These differences were found to be important with the water-accommodated fraction (WAF) in cold water, and significant when reporting the chemically enhanced-water accommodated fraction (CE-WAF), dispersed oil. The differences are chiefly due to the greater accommodation of VOA in the colder water.

Ramachandran et al. (2006) studied the induction of CYP1A enzymes of fish to test the effect of salinity on PAH availability. Freshwater rainbow trout and euryhaline mummichog were exposed to water accommodated fractions (WAF), and chemically-enhanced water accommodated fractions (CEWAF) at 0 o/oo, 15 o/oo, and 30 o/oo salinity. For both species, PAH exposure decreased as salinity increased whereas dispersant effectiveness decreased only at the highest salinity. Risks to fish of PAH from dispersed oil are concluded to be the greatest in coastal waters where salinities are low. The use of chemical oil dispersants causes a transient increase in hydrocarbon concentrations in water, which increases the risk to aquatic species if toxic components become more bioavailable. The risk of effects depends on the extent to which dispersants enhance the exposure to toxic components, such as polycyclic aromatic hydrocarbons (PAH). Increased salinities can reduce the solubility of PAH and the efficiency of oil dispersants.

Shafir et al. (2007) employed a nubbin assay on more than 10,000 coral fragments to evaluate the short- and long-term impacts of dispersed oil fractions (DOFs) from six commercial dispersants, the dispersants and water-soluble-fractions (WSFs) of Egyptian crude oil, on two

Indo Pacific branching coral species. Survivor status and growth of nubbins were recorded for up to 50 days following a single, short (24 hour) exposure to toxicants in various concentrations. Manufacturer-recommended dispersant concentrations proved to be highly toxic and resulted in mortality for all nubbins. The dispersed oil and the dispersants were significantly more toxic than crude oil WSFs. As corals are particularly susceptible to oil detergents and dispersed oil, the authors noted that results of these assays rule out the use of any oil dispersant in coral reefs and in their vicinity. The ecotoxicological impacts of the various dispersants on the corals could be rated on a scale from the least to the most harmful agent, as follows: Slickgone > Petrotech > Inipol > Biorieco > Emulgal > Dispolen.

Of the recent toxicity studies, most researchers (about 75 %) found that chemically-dispersed oil was more toxic than physically-dispersed oil. About half of these found that the cause for this was the increased PAHs (typically about 5 to 10 times) in the water column. Others noted the increased amount of total oil in the water column. Two researchers noted the damage to fish gills caused by the increased amount of droplets. Less than 1/4 of researchers noted that chemically-dispersed oil was roughly equivalent to physically-dispersed oil.

There are some studies departing from the traditional lethal aquatic toxicity assay and also some that focus on the longer-term effects of short term exposures. There certainly is need for more of these types of studies, as the NAS committee on dispersants noted (Committee, 2006). There is also a need to leave the traditional lethal assays and use some of the newer tests for genotoxicity, endocrine disruption and others.

### 3.2.1 Toxicity of Dispersants

Bhattacharyya et al. (2003) carried out toxicity studies in freshwater-marsh-microcosms containing South Louisiana Crude (SLC) or diesel fuel and treated with a cleaner (Corexit 9580) or dispersant (Corexit 9500) using *Chironomus tentans* (benthic invertebrate), *Daphnia pulex* (water flea), and *Oryzias latipes* (fish). Bioassays used microcosm water or soil slurry taken 1, 7, 31, and 186 days after treatment. The crude was less toxic than diesel, chemical additives enhanced oil toxicity, the dispersant was more toxic than the cleaner, and toxicities were greatly reduced by day 186. Toxicities were higher in the bioassay with the benthic species (*Chironomus*) than in those with the two water-column species. Freshwater organisms, especially benthic invertebrates, thus appear seriously effected by the toxicants under the worst-case scenario in the test microcosms.

Koyama and Kakuno (2004) studied the toxicity of three dispersants and heavy fuel oil to a marine fish, red sea bream. The 24-h LC<sub>50</sub> of all three dispersants were at least 1500 mg/L; these dispersants appeared relatively less toxic to marine fish than others studied in the past.

Scarlett et al. (2005) compared the toxicity of the two dispersants, Corexit 9527 and Superdispersant-25 (SD-25), to a range of marine species representing different phyla occupying a wide range of niches: A marine sediment-dwelling amphipod, a mussel, the symbiotic snakelocks anemone and a seagrass. Organisms were exposed to static dispersant concentrations for 48-h and median lethal concentration, median effect concentration, and lowest-observable-effect concentration (LOEC) values obtained. The sublethal effects of 48-h exposures and the ability of species to recover after 72 h after exposure were quantified relative to the 48-h endpoints. Results indicated that the anemone lethality test was the most sensitive with LOECs of 20 ppm followed by mussel feeding rate, seagrass photosynthetic index and amphipod lethality,

with mussel lethality being the least sensitive with LOECs of 250 ppm for both dispersants. The results were consistent with the hypothesis that dispersants act physically and irreversibly on the respiratory organs and reversibly, depending on exposure time, on the nervous system. Superdispersant-25 was found overall to be less toxic than Corexit 9527 and its sublethal effects more likely to be reversible following short-term exposure.

The results of dispersant toxicity testing are similar to that found in previous years, namely that dispersants vary in their toxicity to various species, however, dispersant toxicity is typically less than the toxicity of dispersed oil, by whatever tests. There are no studies departing from the traditional lethal aquatic toxicity assay and none that focus on the longer-term effects of short term exposures. There certainly is need for more of these types of studies. There is also a need to leave the traditional lethal assays and use some of the newer tests for genotoxicity, endocrine disruption and others.

### **3.2.2 Photoenhanced Toxicity**

Several researchers have noted that oil and especially dispersed oil has greater toxicity when exposed to UV or UV components of natural sunlight. Baron et al. (2003) studied the photoenhanced toxicity of weathered Alaska North Slope crude on the eggs and larvae of Pacific Herring with and without the dispersant, Corexit 9527. The oil alone was toxic to larvae at concentrations below 50 µg/L (approximately equivalent to 50 ppb) total PAH (Polycyclic Aromatic Hydrocarbons). Toxicity decreased with time after initial oil exposure. Brief exposure to sunlight of about 2.5 hours/day for 2 days, increased toxicity from 1.5 to 48-fold over control lighting. Photoenhanced toxicity only occurred when oil was present in larval tissue and increased with increasing PAH content in the tissue. Ultraviolet A (UVA) treatments caused a lesser effect than natural sunlight but UVA plus sunlight caused greater toxicity than sunlight alone. The toxicity of chemically-dispersed oil was similar to oil alone in control and UVA treatments, but oil and dispersant treatments were significantly more toxic in the sunlight treatments. The dispersant may be accelerating PAH dissolution into the aqueous phase, resulting in more rapid toxicity. The authors put forward the hypothesis that weathered Alaska North Slope oil is phototoxic and that UV is a factor in the mortality of the early life stages of herring exposed to oil and chemically-dispersed oil.

Kirby et al. (2007) studied the effects of oil on Pacific oyster larvae. Results show that Kuwait crude oil, both mechanically and chemically dispersed, demonstrated significant levels of photo-enhanced toxicity. The mechanically dispersed oil WAF demonstrated toxic effects at 50% dilution under normal laboratory conditions but effects are evident at concentrations as low as 10% under UV conditions. When dispersed oil was tested, effects were apparent at 25% and 5% dilutions under the room and UV conditions, respectively. Comparisons of the no-observed effect concentrations suggest that UV illumination lowers the concentration of the onset of WAF toxicity of Kuwait crude by up to five times and that with dispersed oil the UV-mediated effects are at a point approximately 10 times lower. The impact of UV-light on WAF toxicity is also shown by the calculated LC<sub>50</sub>s with the results showing a 2- and 4-fold increase in toxicity with mechanically and chemically dispersed oil, respectively. These results show that the use of chemical dispersants on oil, increases the toxicity of the WAF and augments the magnitude of the UV-mediated toxicity.

The few tests of photoenhanced toxicity clearly show that oil and especially dispersed oil is



increased by UV light. Increases of 1.5 to 4 fold noted for physically-dispersed oil and from about 4 to 48 times for chemically-dispersed oil. This photoenhanced toxicity is particularly applicable to dispersant application in shallow waters.

### **3.2.3 Testing Protocols**

A group of scientists developed protocols known as CROSERF (Chemical Response to Oil Spills: Ecological Research Forum). The CROSERF aquatic testing protocols were developed with the objective of standardizing test methods and reducing inter-laboratory variability. The purpose of CROSERF was to provide state, federal, and international agencies, industry, academic researchers and consultants engaged in research on the ecological effects of oil spill response chemicals, especially dispersants, with a forum for the exchange of ideas and coordination of research (Aurand and Coehlo, 2005). One of the critical issues in the interpretation of laboratory toxicity data for dispersants and dispersed oil is the lack of standard protocols. As one of the main objectives of CROSERF, the laboratory researchers evaluated ways to improve such tests, and ultimately developed a new set of protocols for conducting toxicity tests, focused on providing consistent detailed analytical chemistry, environmentally realistic exposure regimes, and standard methods for solution preparation. These protocols offer a baseline set of standard procedures which may be used by other laboratories to develop comparable data sets.

Barron and Ka'aihue (2003) reviewed these protocols as they relate to subarctic conditions. A number of refinements were recommended to adapt the protocols to testing with subarctic species with the expected longer oil persistence. These refinements include: testing fresh and moderately weathered oil under conditions of moderate mixing energy, preparing toxicity test solutions using variable duration of tests from 4 to 7 days, quantifying approximately 40 PAHs and their alkyl homologs, assessing the potential for photoenhanced toxicity and incorporating a bioaccumulation endpoint by measuring tissue concentrations of PAHs. Refinements in the preparation of oil dosing solutions, exposure and light regimes and analytical chemistry should increase the utility of the test results for interpreting the toxicity of chemically-dispersed oil in subarctic conditions.

There have been a number of discussions on toxicity testing protocols (Committee, 2006). One note is that the protocols in the oil spill field have not kept pace with the researchers in the field. Another note is that there are many protocols in the literature, and the field of oil spill research appears to still use old protocols largely focused on acute lethal assays.

### **3.3 Biodegradation**

The U.S. National Academy of Sciences reviewed the biodegradation of dispersed oil, noting that the effect of dispersants on biodegradation is a very important topic as one of the stated objectives of using dispersants is to increase biodegradation. The effects of surfactants and oil dispersants on the rate and extent of biodegradation of crude oil and individual hydrocarbons have been extensively investigated with mixed results. In some studies biodegradation is shown to be stimulated, in many there is inhibition and others observed no effects with the addition of dispersants or surfactants. The effect of surfactants and dispersants depends on the chemical characteristics of the dispersants, the hydrocarbons and the microbial community. Other factors such as nutrient concentrations, oil-water ratios and mixing energy also affects the observed

biodegradation rate. Many of the older studies that observed stimulation may have been confounded by the growth on the dispersants themselves as some of the surfactants are readily biodegradable. The effect of the dispersants on the oil biodegradation rate is most sensitive to the characteristics of the dispersant itself, even if all other factors are kept constant. In one study several specific surfactants were shown to inhibit the biodegradation of some classes of hydrocarbons. Only a few surfactants stimulated biodegradation in a culture taken from refinery sludge. NAS noted that other studies have shown complex interactions of oil, surfactant and conditions. One study showed that the ionic surfactant in Corexit 9527 and 9500 inhibited cultures of alkane-degrading bacteria. The non-ionic surfactants in the same mixture stimulated biodegradation. The variable effects of dispersants and surfactants on oil biodegradation are probably due to their effect on microbial uptake of hydrocarbons. It is clear that surfactants can interfere with the attachment of hydrophobic bacteria to oil droplets, making the process very complex to understand. The study concludes that no systematic and reproducible effects of chemical dispersion on the biodegradation rate of crude oil have been demonstrated. The study also notes the experimental systems used to investigate these effects might be inappropriate to represent the environment, because they applied high mixing energy in an enclosed, nutrient sufficient environment and allowed sufficient time for microbial growth. Microbial growth on open-ocean slicks is likely to be nutrient limited and may be slow relative to processes that lead to the formation of water-in-oil emulsions, which are resistant to biodegradation. It also noted that the most toxic components of the oil, the biodegradation of PAHs, have never been shown to be stimulated by dispersants. The study concludes that only PAH mineralization can be equated with toxicity reduction, stimulation of alkane biodegradation would not be meaningful in the overall toxicity of oil spills (Committee, 2006).

Lindstrom and Braddock (2002) examined the effects of Corexit 9500 and sediment on microbial mineralization of specific aliphatic and aromatic hydrocarbons found in crude oil. The gross mineralization of crude oil, dispersed crude oil and dispersant by a marine microbial consortium in the absence of sediment was also measured. When provided as carbon sources, the chosen consortium mineralized Corexit 9500 the most rapidly, followed by fresh oil, and finally weathered oil or dispersed oil. However, mineralization in short term assays favored particular components of crude oil (2-methyl-naphthalene > dodecane > phenanthrene > hexadecane > pyrene) and was not affected by addition of nutrients or sediment. Adding dispersant inhibited hexadecane and phenanthrene mineralization but did not affect dodecane and 2-methyl-naphthalene mineralization. Thus, the effect of dispersant on biodegradation of a specific hydrocarbon was not predictable by class but included inhibition.

Page et al. (2002) conducted an experiment at a wetland research facility, to investigate the behavior and effects of chemically dispersed oil (CDO) using Corexit 9500. The replicated treatments included oiled control, “high-dose” CDO (1:10 dispersant-to-oil ratio (DOR)), low-dose CDO (1:20 DOR), as well as an unoiled control. Known amounts of oil or dispersed oil were added to the respective plots. Sediment samples were taken over a 99-day period using a 5-cm-diameter coring device. The GCMS results for both total target saturate hydrocarbons and total target aromatic hydrocarbons were measured and data were modeled using nonlinear regression. The overall (including abiotic and biotic) petroleum loss rates for the dispersed-oil treatments were not statistically different when compared to the oiled control. However, the initial concentrations for the dispersed-oil treatments were statically lower than for the oiled control.

From this, it can be inferred that the dispersed oil was more prone to flush off the sediments, as was visually observed. Biodegradation rates were also determined for all treatments; it was concluded that there were no differences when comparing each dispersed-oil treatment to the oiled control. The sediments from each plot were also analyzed for microbial population numbers and acute toxicity. Statistical analyses for both sets of data found no significant differences for the dispersed-oil treatments when compared to the oiled control.

MacNaughton et al. (2003) studied the degradation of crude oils, with and without dispersant was carried out as two separate experiments, without replication. In one experiment Forties crude was mixed with a dispersant, Corexit 9500, and nutrients and incubated for 27 days at 15°C. In another, experiment Alaska North Slope, treated similarly, was incubated at 8°C for 35 days. All results were compared to a 'killed' control with no nutrients added. A third test was carried out in which only seawater was added and no dispersant. The test vessel was similar to the Mackay dispersant apparatus with a high air flow. The amount of total alkanes was measured in the samples. In both studies microbial colonies started after 4 days as well as the formation of neutrally-buoyant clusters consisting of oil, bacteria, protozoa and nematodes. By day 16, the sizes of the clusters increased and sank to the bottom of the test flask. In the 'killed' controls, no bacteria were observed. The TPH measurements in all three tests showed similar end results, with the dispersant one being slightly lower in the Forties case, but not in the Alaska oil case. No biodegradation was observed in the Alaska oil some was apparent in the Forties oil.

Martha and Mulligan (2005) carried out a comparison in biodegradability of oil with dispersants or biosurfactants. A Brent crude, Corexit 9500 and a biosurfactant were used. The biosurfactant, rhamnolipid is a metabolic by-product of *Pseudomonas aeruginosa*. The commercial product, JBR 425, in a 25% solution, was used. The EPA biodegradation protocol using a 250 mL flask was employed. Five treatments were compared for total GCMS TPH and microbial counts over the 35 day experiment. The treatments were oil only, chemical dispersant, bio-dispersant, a biological agent (seeded solution) and bio-dispersant with the biological agent. The most biodegradation occurred with the bio-dispersant and biological agent mixed, then the biological agent alone, then the bio-dispersant, then oil only and then finally with the dispersant only. The measurement of microbial counts showed about the same order of populations. It was concluded that the use of the rhamnolipid biosurfactant promoted biodegradation whereas the chemical dispersant always suppressed biodegradation.

Yoshida et al. (2006) studied microbial responses to the addition of oil with or without a chemical dispersant were examined in mesocosm and microcosm experiments by using denaturing gradient gel electrophoresis of bacterial ribosomal DNA and direct cell counting. When a water-soluble fraction of oil was added to seawater, increases in cell density were observed in the first 24 h, followed by a decrease in abundance and a change in bacterial species composition. After addition of an oil-dispersant mixture, increases in cell density and changes in community structure coincided, and the amount of bacteria remained high. These phenomena also occurred in response to addition of only dispersant. These results suggest that the chemical dispersant may be used as a nutrient source by some bacterial groups and may directly or indirectly prevent the growth of other bacterial groups. Thus overall, the effect of dispersant overall may be to slow biodegradation depending on the type of bacteria present.

Nyman et al. (2007) set up microcosms to measure the effects of chemical additives on hydrocarbon fate in freshwater marshes. The test microcosms received no hydrocarbons, South

Louisiana crude, or diesel; and no additive, a dispersant, or a cleaner. Oil fate was determined the concentration of four total petroleum hydrocarbon (TPH) measures and 43 target hydrocarbons in water and sediment fractions 1, 7, 31, and 186 days later. Disappearance was distinguished from biodegradation via hopane-normalization. After 186 days, TPH disappearance ranged from 24% to 97%. There was poor correlation among the four TPH measures, which indicated that each quantified a different suite of hydrocarbons. Hydrocarbon disappearance and biodegradation were unaltered by these additives under worse-case scenarios. There was generally no benefit in increased biodegradation nor a significant decline in degradation. The authors conclude that use of these additives must generate benefits that outweigh the lack of effect on biodegradation demonstrated in this report, and the increase in toxicity that they reported earlier.

Venosa and Holder (2007) conducted laboratory experiments to study the biodegradability of oil after dispersants were applied. Two experiments were conducted, one at 20°C and the other at 5°C. In both experiments, only the dispersed oil fraction was investigated. Each experiment included treatment flasks containing 3.5% artificial seawater and crude oil previously dispersed by either Corexit 9500 or JD2000 at a dispersant-to-oil ratio of 1:25. Two different concentrations of dispersed oil were prepared, the dispersed oil then transferred to shake flasks, which were inoculated with a bacterial culture and shaken on a rotary shaker at 200 rpm for several weeks. Periodically, triplicate flasks were removed and sacrificed to determine the residual oil concentration remaining at that time. Oil compositional analysis was performed by gas chromatography/mass spectrometry to quantify the biodegradability. Dispersed oil biodegraded rapidly at 20°C and less rapidly at 5°C. After time, the rate of biodegradation of the undispersed oil was about the same as dispersed oil.

Al-Sarawi et al. used water samples from the Kuwait coast to count and isolate bacteria capable of growth on low molecular weight organic compounds known to be released by picocyanobacteria. The compounds tested were potassium acetate, sodium pyruvate, fumaric acid, succinic acid, sodium citrate and glycerol. For comparison, the bacterial numbers on glucose and Tween 80 and crude oil (Tween 80 is a surfactant related to those sometimes used in dispersants), as sole sources of carbon and energy were also determined. Sodium pyruvate was, in most cases, the carbon and energy source most commonly utilized by the cultivable surface water bacteria. Four common cultivable bacterial genera and three less common bacterial genera were identified on the test carbon sources. Quantification of heterotrophic bacteria associated with cultures of local picocyanobacterial strains, originally isolated from the Gulf surface water, also revealed that the carbon source most commonly utilized by cultivable bacteria was sodium pyruvate. Bacteria were not countable on the oil or Tween, indicating that these were not a preferred source of carbon and would be degraded after sodium pyruvate, if at all.

Overall, one might note that many of the experimental systems used to investigate these effects might be inappropriate to represent the environment, because they applied high mixing energy in an enclosed, nutrient sufficient environment and allowed sufficient time for microbial growth. Microbial growth on open-ocean slicks is likely to be nutrient limited and may be slow relative to other fate processes, many of which are resistant to biodegradation. It also noted that the most toxic components of the oil, the biodegradation of PAHs, have never been shown to be stimulated by dispersants (Committee, 2006). The study concludes that only PAH mineralization can be equated with toxicity reduction, stimulation of alkane biodegradation would not be meaningful in the overall toxicity of oil spills.

Of the recent studies noted about, about half of the researchers noted inhibition of oil biodegradation by dispersants and the other half found that biodegradation rates were about the same.

## **4 Other Issues**

### **4.1 Component Separation**

It has been known for a long time that there is some oil component separation with the use of dispersants. Abdallah et al. (2005) noted this separation for a light Middle East crude and four different dispersants. This study of dispersion and analysis by gas chromatography showed that the lower n-alkanes are much more dispersed than are other components including the larger n-alkanes.

### **4.2 Dispersant Use in Recent Times**

Henry (2005) reviewed the seven spills in the Gulf of Mexico between the years of 1995 and 2005 which were treated with dispersants. The spills are: West Cameron 198 Pipeline spill, 1995; High Island Pipeline system Oil Spill, 1998; T/V Red Sea Gull spill, 1998; Mississippi Canyon 109 Pipeline Spill, 1998; M/V Blue Master, 1999; Poseidon Pipeline Oil Spill, 2000; and Main Pass 69 Pipeline Spill, 2004. It is concluded that although these applications appeared to be successful, little measurement or documentation took place.

Payne and Allen (2005) conducted laboratory tests with the Santa Barbara seep oil. Results from those tests indicated that the 11° API gravity seep oil from the Monterey Formation was not amenable to treatment with dispersants (0% dispersion), but similar tests on nearby Platform Holly produced oil (also from the Monterey Formation) indicated a possible dispersion of up to 70%. A limited set of *in situ* field tests (using a hand-held spray bottle with less than one pint of Corexit 9500) were completed on the seep oils in June 2003 to determine if the earlier laboratory results were an artifact of the seep oil collection and shipment or some other unknown factor. The field tests convincingly demonstrated that the natural seep oils were not amenable to treatment with Corexit 9500.

Gilson (2006) reports on the use of dispersants on the Exxon Valdez spill. Within hours of the Exxon Valdez spill, the United States Coast Guard (USCG) discussed dispersant use with Alyeska and others. A trial run performed on the first day of the spill was determined to be ineffective. Massive herding was observed by the application crew. The effectiveness of two subsequent drops was inconclusive because of poor light and mechanical problems. The fourth drop had increased wave action that theoretically could have helped mix the dispersant. Increased winds hampered the fifth and sixth drops, and it was determined that the window for effectiveness had closed. The remaining four experimental applications in Blying Sound on April 2 and April 13 off Seward were ineffective due to the emulsification of the oil.

Chapman et al. (2007) reviewed the use of dispersants on oil spills that occurred over the 10 year period in Europe between 1995 and 2005 and noted that there were relatively few occasions when dispersants were used in response to incidents in European waters. This appears to be chiefly due to unfavorable circumstances for dispersants to work effectively. Of the 77 incidents attended by ITOPF in Europe during the period under review, 6 involved the use of dispersants at sea (8%): one in France, one in Cyprus, two in Greece and two in the UK. Two of the six incidents were spills of heavy fuel oil.

Steen and Findlay (2008) reviewed the published literature on dispersant use around the world shows 213 documented uses since 1968 and 38 in the last decade. Overall, about 50% of the events were noted as being effective and the other half about equally ineffective or inconclusive, or undocumented. Use is now highest in Africa and Asia. The reporting of use is noted as being inconsistent and in some cases, absent.

In summary, dispersant use in recent times is not well-documented or is in fact, decreasing. Scientific assessment of dispersant effectiveness at spill scenes is often not carried out.

#### **4.3 Assessment of the Use of Dispersants**

The NAS committee on the study of dispersants (Committee, 2006) commented on dispersant assessment overall. The committee notes the context of dispersants within oil spill countermeasures. Dispersants might be used if: (a) an oil slick threatens a sensitive coastal area and mechanical recovery is not feasible, (b) there is sufficient wave energy to break up the surface slick and mix the oil droplets into the water column, c) the oil is of a type known to be dispersible, (d) there is sufficient potential for rapid dilution of the dispersed oil, and (e) in the course of spraying, dispersants are not applied directly to birds or mammals. The report notes that there is insufficient scientific information upon which to make decisions about likely benefits and consequences of dispersant use as an oil spill countermeasure. The report also notes that there is disagreement about how to interpret the results of laboratory, mesocosm and limited field tests to date, because of the difficulty of simulating an adequate range of realistic exposure conditions. The report also notes that there remain basic issues that need to be resolved before dispersants are more fully accepted as a response tool. Examples of these include the sensitivity of effectiveness to environmental factors and oil properties. This change cannot be accurately predicted with sufficient consistency to support decision-making over a variety of conditions. Another example given is that the acute and chronic toxicity of dispersed oil has not been adequately studied under realistic conditions to support decision-making and risk balancing. With respect to near-shore dispersion, it notes that there is a lack of sufficient information regarding effectiveness and potential effects over a wide range of conditions found in nearshore areas, to enable a policy decision on such use.

The committee also reviewed the decision-making process in the USA (Committee, 2006). Three approval processes are in place, case-by-case approval, quick approval and preapproval. In each case, the use of dispersant would require the federal on-scene commander to have approval from the regional response team. Before decisions are made, there are three basic questions: will dispersants work?, can the spill be treated effectively?, and what are the environmental trade-offs? A major consideration in decision-making would also include the preparedness to apply dispersants in adequate quantity. New U.S. Coast Guard rules require the ability to apply dispersants within 12 hours after an oil release within 50 nautical miles of shore. Considerations should also include adequate supply of dispersants and the ability to apply at a dispersant:oil dosage of 1:20. The risk framework includes 3 phases, problem formulation or definition, analysis and risk characterization. The problem definition phases includes: identifying habitats and resources of concern, identifying stressors and response options, and identifying resource interactions. The analysis phase would include: use of a trajectory model to predict what habitats might be impacted, assessment of scientific literature, discussion on estimates and preparation of a risk square, a tool to weight the various risks and options. This analysis should take place before

any spill and the information would be available to the parties requiring it. Because spill conditions may deviate from the set of scenarios used, real-time decision-making may be necessary. Further questions might be asked: will mechanical response be sufficient?, is the spilled product known to be dispersible?, are sufficient chemical response assets available to treat the spill?, are the environmental conditions conducive to successful application and effectiveness?, and will the effective use of dispersant reduce the impacts of the spill to shoreline and water surface resources without significantly increasing impacts to water column and benthic resources?

Many workshops have been held on the assessment for the use of dispersants (Aurand, 2003; Aurand and Coehlo, 2003, 2004, 2005, 2006, 2007; Belore, 2004). Several manuals also have been issued in this time period (Cedre, 2005; Fingas, 2006; Lewis et al., 2006 and UK Institute of Petroleum, 2004).

#### **4.4 Spills-of-Opportunity Research**

The U.S. National Academy of Sciences notes that spills-of-opportunity may provide a good opportunity to conduct needed research (Committee, 2006). Their report recommends the following: detailed plans, target areas on the surface need to be identified by smoke bombs or other markers, dispersant to be applied into the wind, good photo and video documentation, water column concentrations measured with fluorometers and grab samples by GCMS, and use of remote sensing techniques. It is also recommended that both dissolved-phase and particulate oil droplets be sampled. Disadvantages of spills-of-opportunity studies include the fact that needed resources are often tied up in response thus scientific operations may not be possible.

Good data from real spills would be most useful in making assessments and inputs for spill models. Essential data needs include: concentrations under the water column, effectiveness values, diffusion and transport values with currents and winds, separation between dissolved and droplet components, long-term data and detailed component analysis of the dispersed oil with time.

#### **4.5 Interaction with Sediment Particles**

The NAS Academy report notes that not much is known about the long-term fate of oil and SPM in the water column (Committee, 2006). Once formed oil-mineral aggregates appear to be very stable structures and the buoyancy will depend on the oil to mineral ratio. In one study, more oil settled to the bottom in the absence of dispersants than with dispersants. A study also noted that increased clay concentrations were needed to form aggregates as the salinities increased. Dispersant treatment results in greater numbers of oil droplets and thus greater number of interactions with SPM and greater number of agglomerates. The greater number of mineral particles results in larger and more aggregates. It should be noted that large amounts of research have been conducted on oil-SPM interaction since the NAS report was completed and there are many findings, notably that oil-SPM particles will often settle to the bottom.

Khelifa et al. (2008) studied aggregation between suspended oil droplets and suspended particulate matter (SPM), which leads to the formation of oil-SPM aggregates (OSAs). A laboratory study was conducted to measure the size, density and settling velocity of OSAs formed under various mixing conditions. Both physically and chemically dispersed oils were tested using Standard Reference Material 1941b prepared by the National Institute of Standards and

Technology, Arabian Medium and South Louisiana crude oils, and Corexit 9500 dispersant. Two sediment-to-oil ratios of 0.5 and 1 were used. At a sediment-to-oil ratio of 0.5, the results showed that oil-SPM interaction leads to formation of abundant negatively-buoyant OSAs that settle at an average rate of 1 mm/s, their average effective density is about 60 g/L and their size varies from 30 to about 350  $\mu\text{m}$ . The minimum effective density and settling velocity of OSAs measured in this study were 34 g/L and 0.3 mm/s, respectively. Slightly denser OSAs were obtained with chemically dispersed oil. Less difference was obtained between physical properties of OSAs and those of sediment flocs when the sediment-to-oil ratio was increased from 0.5 to 1. Both the Stokes' Law and a modified one overestimate the settling velocity of OSAs and are not recommended for use in oil spill modeling.

Li et al. (2008) conducted a wave tank study to investigate the effects of chemical dispersants and mineral fines on the dispersion of oil and the formation of oil-mineral-aggregates (OMAs) in natural seawater. Results of ultraviolet fluorometry and GC-FID analysis indicated that dispersants and mineral fines, alone and in combination, enhanced the dispersion of oil into the water column. Measurements taken with a laser in-situ scattering transmissometer showed that the presence of mineral fines increased the total concentration of the suspended particles from 4 to 10  $\mu\text{L/L}$ , whereas the presence of dispersants decreased the particle size (mass mean diameter) of OMAs from 50 to 10  $\mu\text{m}$ . Observation with an epifluorescence microscope indicated that the presence of dispersants, mineral fines, or both in combination significantly increased the number of particles dispersed into the water.

In summary, the interaction of droplets, particularly chemically-dispersed droplets appears to be an important facet of oil fate. Although much more research is needed, it appears that high concentrations of sediment will have significant effect on dispersed oil droplets and the formation of stable OMAs. These OMAs will sink slowly and sediment on the bottom.

#### **4.6 Modeling Oil and Dispersed Oil Behaviour and Fate**

The U.S. Academy committee conducted fourteen model runs using two different oil spill models to assess the sensitivity and effect of various input parameters on various outputs including fate, trajectory, encounter with a shoreline, etc. (Committee, 2006). The scenarios were found to be instructive, however the need to specify dispersant effectiveness as a model input is the weakest part of the dispersant assessment. Unfortunately, the dispersant effectiveness is one of the most important input parameters. The results of the exercise indicate that without models, it is very difficult to integrate all interacting (and perhaps competing) transport and fate process, oil properties and dispersant use to predict the oil in various compartments and in various areas. It is concluded that transport and fate models should be used to assist in making decisions during an actual spill. This is especially the case in the nearshore where there are even more complex flow fields. Models require improvement and efforts should be made to improve and validate models. This includes undertaking research at laboratory and meso-scale to define the parameters that control oil dispersibility.

Several efforts have been carried out to predict overall response costs, effects, and resource damage with various levels of dispersant effectiveness (Etkin et al., 2002; French-McCay et al., 2001, 2005, 2006, 2008; Reed et al., 2004; Schmidt-Etkin 2003, 2005). The limitations of this modeling are, as noted by the committee: effectiveness must be assumed and input, the effectiveness with time is not calculated, and inputs for various fates and effects are not



necessarily available. The exercises are useful, however, to understand the various facets of response, resource assessment and costs.

#### **4.7 Dispersed Oil Stability and Resurfacing**

The literature confirms the well-known phenomenon that chemically dispersed oil destabilizes after the initial dispersion (Fingas and Ka'ahue, 2006; Fingas 2008). The destabilization of oil-in-water emulsions such as chemical oil dispersions is a consequence of the fact that most emulsions are not thermodynamically stable. Ultimately, natural forces move the emulsions to a stable state, which consists of separated oil and water. The rate at which this occurs is important. An emulsion that stays sufficiently stable until long past its practical use consideration may be said to be kinetically stable. Kinetic stability is a consideration when describing an emulsion. An emulsion is said to be kinetically stable when significant separation (usually considered to be half or 50% of the dispersed phase) occurs outside of the usable time.

There are several forces and processes that result in the destabilization and resurfacing of oil-in-water emulsions such as chemically dispersed oils. These include gravitational forces, surfactant interchange with water and subsequent loss of surfactant to the water column, creaming, coalescence, flocculation, Ostwald ripening, and sedimentation.

Gravitational separation is the most important force in the resurfacing of oil droplets from crude oil-in-water emulsions such as dispersions and is therefore the most important destabilization mechanism. Droplets in an emulsion tend to move upwards when their density is lower than that of water. This is true for all crude oil and petroleum dispersions that have droplets with a density lower than that of the surrounding water. More dense oils, which would sink as emulsions, are poorly, if at all, dispersible. The rate at which oil droplets will rise due to gravitational forces is dependent on the difference in density of the oil droplet and the water, the size of the droplets (Stokes' Law), and the rheology of the continuous phase. The rise rate is also influenced by the hydrodynamical and colloidal interactions between droplets, the physical state of the droplets, the rheology of the dispersed phase, the electrical charge on the droplets, and the nature of the interfacial membrane.

Creaming is the destabilization process that is simply described by the appearance of the starting dispersed phase at the surface, without the processes in the intervening spaces being described. In the oil spill world, creaming is the process that might be described as resurfacing.

Coalescence is another important destabilization process, which has been studied extensively in oil-in-water emulsions. Two droplets that interact as a result of close proximity or collision can form a new larger droplet. The end result is to increase the droplet size and thus the rise rate, resulting in accelerated destabilization of the emulsion. Studies show that coalescence increases with increasing turbidity as collisions between particles become significantly more frequent.

Ostwald ripening is another process in the destabilization of oil-in-water emulsions. Ostwald ripening occurs when the larger droplets in an emulsion grow due to absorption of soluble components or very small droplets from the water column. The effect is to remove soluble material from the water column and smaller droplets, resulting in an increased growth of the larger droplets. The phenomenon occurs because the soluble components of the dispersed phase are more soluble in the larger droplets than in the water and the smaller droplets. Although the Ostwald ripening phenomenon has not been investigated with oil-in-water emulsions to the same extent as other phenomena, it is believed to be important.

Another important phenomenon when considering the stability of dispersed oil is the absorption/desorption of surfactant from the oil/water interface. This process is stated to be the most important process for chemical considerations of surfactants and interfacial chemistry. When surfactants are dissolved in a bulk phase such as water, they start to be absorbed at the oil surface or interface. The system moves toward equilibrium, that is equilibrium amounts of surfactant at the interface and in the bulk phase. Desorption occurs primarily as a result of the lower concentration of surfactants in the bulk phase or water. The surfactants will transfer back and forth from the oil/water interface until an equilibrium of concentration is established in the interface or in the bulk liquid (water). It is well known that in dilute solutions, much of the surfactant in the dispersed droplets ultimately partitions to the water column and thus is lost to the dispersion process. Little, if any, surfactant would partition back into the droplet in a dilute solution, which is the case for oil dispersions at sea. This is one important difference between dilute and concentrated solutions. This report provides examples of studies and models in all the processes as well as data from experiments and calculations. Data show that for a dilute solution such as a chemically dispersed oil spill, half-lives could vary from 2 to 24 hours, with a typical average value of 12 hours.

Sterling et al. (2004) performed thermodynamic and kinetic investigations to determine the influence of coalescence of chemically dispersed crude oil droplets in saline waters. For the range of pH (4–10) and salinity (10‰, 30‰, 50‰) values studied,  $\zeta$ -potential values ranged from -3 to -10 mV. As the interaction potential values calculated using Derjaguin–Landau–Verway–Overbeek (DLVO) theory were negative, the electrostatic barrier did not produce significant resistance to droplet coalescence. Coalescence kinetics of premixed crude oil and chemical dispersant were determined within a range of mean shear rates ( $G$  ¼, 5, 10, 15, 20 s<sup>-1</sup>) and salinity (10‰, 30‰) values. Coalescence reaction rates were modeled using Smoluchowski reaction kinetics. Measured collision efficiency values ( $\alpha = 0.25$ ) suggest insignificant resistance to coalescence in shear systems. Experimentally determined dispersant efficiencies were 10–50% lower than that predicted using a non-interacting droplet model ( $\alpha = 0.0$ ). This confirms the literature findings that coalescence is increased by increasing turbidity. Unlike other protocols in which the crude oil and dispersant are not premixed, salinity effects were not significant in this protocol. This approach allowed the effects of dispersant–oil contact efficiency to be separated from those of water column transport efficiency and coalescence efficiency.

In summary, the NAS committee on dispersants (2006), along with many researchers, recognized that oil spill dispersions are not stable and that dispersed oil will destabilize and rise to the surface. Half-lives of dispersions may be between 4 to 24 hours. More study on this is needed and this consideration requires to be incorporated into dispersant effectiveness studies.

#### **4.8 Separation of Dispersants from Water**

After a dispersant test, much of the applied dispersant is in the test water and oil can be removed by surface methods. In large test tanks, the water cannot be replaced so means are needed to remove excess surfactants. Cooper et al. (2003) showed that this can be carried out using membrane or reverse osmosis techniques, however this method is not very economical. SLR (2003) also showed that activated carbon works for this purpose and this is the method now used.

#### **4.9 Dispersant Breakthrough Oil Slicks**

It is known that dispersant droplets can break through oil slick and then herd the oil. To date no test has been conducted of the droplet sizes to break through typical oils that might be dispersed. Ebert et al. (2008) carried out a test on IFO-380 and found that 1000 µm droplets did not break through a thin slick of this material. But since IFO-380 is highly elastic and not considered to be dispersible, tests on dispersible oils are needed.

#### **4.10 Overall Effects of Weather on Dispersion**

Fingas and Ka'ahue (2004) studied how oil spill countermeasures are affected by weather. A literature review was carried out to determine if there were data related to the performance of all countermeasure techniques under varying weather conditions. Although the literature did not provide any quantitative guides for the performance of countermeasures under varying weather conditions, data could be extracted to enable assessment of changes in their performance related to weather conditions. The most important factors influencing countermeasures are wind and wave height. These two factors are related and, given sufficient time for the sea to become 'fully-arisen', can be inter-converted. These factors must sometimes be considered separately so that specific weather effects can be examined. Other weather conditions affecting countermeasures include currents and temperature. Currents are important as they become the critical factor for certain countermeasures such as booms. Temperature primarily affects the performance of dispersants and has been shown to have only minimal effect on other countermeasures. The weather affects dispersant application and effectiveness in three ways: the amount of dispersant that contacts the target is highly wind-dependent; the amount of oil dispersed is very dependent on ocean turbulence and other energy; and the amount of oil remaining in the water column is dependent on the same energy. At high sea energies, natural dispersion is very much a factor for lighter oils.

Nuka Research (2008) carried out a study on weather windows for Prince William Sound and this study indicates that:

- Dispersant application in the Central Sound is not possible 75% of the time year-round, mostly because of darkness and conditions too calm for dispersant mixing.
  - Dispersant application at Hinchinbrook Entrance is not possible 80% of the time year-round, mostly because of darkness, conditions too rough for application, or too calm for mixing.
- These were compared with the results of the mechanical response gap estimate for the same two operating areas of Prince William Sound, concluding:
- When all technologies are considered together, some type of response can be mounted in Central Prince William Sound 90% of the time and 70% of the time at Hinchinbrook Entrance.
  - Mechanical Response is a more robust response technology than either dispersants or in-situ burning in both operating areas. Mechanical response is the response method least likely to be precluded by environmental conditions in both the Central Sound and Hinchinbrook Entrance areas.
  - Overall, response in either area is more likely to be precluded by environmental factors in winter than in summer.

In summary, weather including temperature, winds and waves are an important consideration for oil spill dispersion. The weather 'window' for effective dispersant use may be small in northern areas.

#### **4.11 Joint Effect of Temperature and Salinity on Effectiveness**

Fingas et al. (2006) studied dispersion effectiveness for Alaska North Slope oil at different temperatures and salinity has been measured. The results of this were compared to a historical test reported in the literature, in which both the temperature and salinity were varied over a range of values. The finding of this study is that there is an interaction between salinity and effectiveness for Alaska North Slope crude oil.

Fingas and Ka'aihue (2005) reviewed literature on the effects of water salinity on chemical dispersion, especially those effects related to effectiveness. Literature shows that testing of effectiveness with salinity variation consistently shows a decrease in effectiveness at lower salinities and a decrease after a maximum salinity is reached between about 20 to 40 o/oo. There is a body of literature on the use of surfactants for secondary oil recovery. There are some commonalities among the many findings. Recovery efficiency falls off at both high and low salinities. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant. Several studies on the interaction of specific hydrocarbons and surfactants were reviewed. The consensus is that the solubility of the hydrocarbon increases with increasing salinity and is low at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25 to 35 o/oo. A number of physical systems involving surfactants and salinity changes are reported in the literature. Included in these is the finding that the stability of microemulsions is greater at salinities of 25 to 35 o/oo. Some workers found that the stability of systems was very low in fresh water or in water with salinities of < 10 o/oo. This is consistent with the findings in the oil spill literature.

In summary, there appears to be an interaction between salinity and temperature for oil spill dispersant effectiveness. Effectiveness appears to peak at about 15°C and about 25o/oo. Further study in other test apparatuses is suggested.

#### **4.12 Monitoring Dispersant Effectiveness at Actual Spills**

The purpose of monitoring is to determine if a dispersant application was relatively effective or not; to provide information to the responders and to provide scientific information for decision-making and modeling. The most common protocol now is the SMART monitoring protocol from a number of USA government agencies. The protocols currently consist of some visual criteria and often include a sub-surface monitoring program consisting of using in-situ fluorometers to gauge the relative effectiveness of a dispersant application. It should be noted that there are no monitoring guidelines in SMART or many other protocols. Some types of biological monitoring, it is felt, are needed.

There are many false positives and false negatives with both monitoring techniques (Fingas and Ka'aihue, 2004, Committee, 2006). These can be overcome by paying attention to the science and technology. 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. There are more methods described in the literature that can yield more information (Fingas and Ka'aihue, 2004). 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 and the timing of the analytical results.

In summary, effectiveness monitoring at actual dispersant operations could provide very useful information for future assessment, modeling and basic understanding of chemical dispersion. Emphasis must be placed on obtaining accurate and precise data.

#### **4.13 Correlation of Dispersant Effectiveness with Oil Properties.**

Several workers have found that specific oil properties correlate well with dispersant effectiveness measures in the laboratory.

Fingas et al. (2003) used dispersant effectiveness data on 295 oils and their chemical and physical properties and these correlated with 29 properties to develop a prediction equation. The dispersibility of Corexit 9500 in the swirling flask apparatus was used as the key parameter. The highest correlation parameters were achieved with the content of nC12, naphthalenes, inversely with C26, the PAHs, and the sum of C12 to C18 hydrocarbons. This is highly indicative that the smaller aliphatic hydrocarbons up to C18 and the PAHs are the most dispersible components of oil. Furthermore, aliphatic hydrocarbons greater than C20 correlate inversely with the dispersant effectiveness, indicating that these hydrocarbons suppress dispersion. Thirteen models were constructed to predict the chemical dispersibility of oils. The simplest and best model is:  $\text{Corexit 9500 dispersibility (\%)} = -11.1 - 3.19(\ln \text{C12 content}) + 0.00361(\text{naphthalene content in ppm}) - 7.62(\text{PAH content squared}) + 0.115(\text{C12 to C18 content squared}) + 0.785(\% \text{fraction oil boiling below } 250^{\circ}\text{C})$ . Models ranged from simple predictors involving only two parameters such as viscosity and density to 14-parameter models. The models developed were analysed statistically and the effectiveness was calculated for several dispersants. The more sophisticated models are able to predict dispersant effectiveness with high accuracy.

Belore (2007) correlated effectiveness with some SARA components for the U.S. Gulf oils. Weaver (2008) correlated effectiveness in the baffled flask with various U.S. oils.

Limited studies show good correlation with oil properties and dispersant effectiveness. The more specific the chemical property, the better the correlation.

#### **4.14 Dispersibility of Biodiesels**

Hollebone et al. (2008) examined natural and chemically-enhanced dispersion of biodiesel in both low- and high-energy conditions. Biodiesels were found to have significant differences with petroleum diesels in water chemistries and in potential ecological impacts. All organisms tested show that biodiesels have less acute toxicity than petroleum diesels. It remains unclear which components of the biodiesels are the most water-soluble and have the greatest potential for adverse effects on aquatic ecosystems. Neat biodiesels were found to be much more dispersible in high-energy conditions than petroleum diesel.

#### **4.15 Application Systems**

Some work on application systems was carried out. Motolenich and Clark reviewed vessel dispersant application systems. Three types of vessel application systems are noted: spray arm

systems, fire monitor systems and single nozzle neat application systems.

Salt et al. (2003) reviewed new strategies for the deployment of dispersants using aircraft. The development of alternative small-aircraft packages are summarized.

Nedwed et al. (2007) discussed the use of icebreakers to mix oil spill dispersions in ice conditions. Testing of this concept was carried out in a basin with ice present and shows effective dispersion occurred. The mixing extends up to 20 m below the icebreaker.

Nedwed et al. (2008) described a new dispersant that is a gel. The dispersant has up to 90% active ingredient compared to 40 to 50 % for traditional dispersants. The concept is the buoyant gel will float and mix with the oil, rather than being washed off as many traditional dispersants. Preliminary testing with the dispersant showed that it more effective on more viscous oils and is effective at lower dispersant:oil ratios. Further, aerial application is thought to be more successful with less drift.

There are several ASTM standards on dispersant application. Of most significance during the time period of this literature review is the new standard on single-nozzle neat application systems (ASTM, 2007).

## **5 Recommendations for Further Research**

The NAS committee's recommendations for further research can be summarized: field-scale work should be based on coordinated bench-scale and wave-tank testing; conduct a research program to identify the mechanisms and rates of weathering processes that control dispersant effectiveness and include well-coordinated bench scale and wave-tank experiments; conduct a research program to provide data necessary to model chemical, environmental and operational effectiveness of dispersant application including nearshore situations; models should be improved, validated and validated during experimental spills or during an actual spill; a series of experiments is needed to quantify weathering rates and fate of chemically-dispersed oil droplets compared to undispersed oil; conduct modeling and associated biological assessments with and without dispersants to develop operation envelopes of dispersant use for oil types, volumes and types of water bodies; conduct focused studies to provide data to predict photo-enhanced toxicity, estimate relative contribution of dissolved and particulate oil phases to representative species toxicity and include an evaluation of delayed effects; ensure that the spill response community is aware of developments in the broad field of ecotoxicology and the various tools developed; and conduct studies to assess the ability of fur and feathers to maintain the water-repellency critical for thermal insulation under dispersed oil exposure conditions.

CRC held a workshop to discuss dispersant research priorities (CRC, 2006). Overall, the priorities that were recommended by the participants were complementary to the NRC recommendations. There were common action items identified:

- Expansion of data-mining and literature syntheses for efficacy and effects,
- Improvement in designing studies and analytical protocols to allow better inter-comparisons among studies,
- A return to bench-scale testing to fill basic gaps that still exist,
- Better field monitoring methods and technologies at spills of opportunities, and
- Development of integrated models to assist decision makers on dispersant use during planning and emergency response.

More specifically the following general areas were recommended for study (CRC, 2006):

1. Efficacy of dispersants
  - a) Literature synthesis on physical and chemical properties of oils that determine the overall effectiveness of dispersant application
  - b) Protocols for creating weathered oil/emulsions
  - c) Provide data for decision makers to better predict the dispersibility of a less-studied oil by comparison of its properties with a series of well-studied standard oils
  - d) Development and inter-comparison studies of methods for measuring droplet size distributions and energy dissipation rate in different dispersant effectiveness test systems
  - e) Design and implement a research program to fill identified data gaps in chemical dispersant effectiveness testing
  - f) Determination of the factors that represent realistic operational conditions for wave tank test systems
2. Operational and Hydrodynamic Parameters that Influence Overall Effectiveness
  - a) Improving models of dispersed oil transport in the upper mixed layer
  - b) Update SMART monitoring protocols
  - c) Assessment of the effects of dispersant application on subsequent mechanical recovery of undispersed oil
  - d) Optimizing the operational effectiveness of dispersant applications
  - e) Evaluation of new technologies for monitoring dispersant effectiveness in the field
3. Modeling Integration of Chemical, Operational and Hydrodynamic Parameters
  - a) Workshop on requirements for integrating oil toxicity and biological data with oil fate and transport models
  - b) Improved models to predict dispersant effectiveness and oil fate
4. Fate of Oil and Dispersed Oil in the Water Column and Other Habitats
  - a) Understanding the interactions of chemically dispersed oil droplets with suspended particulate matter (SPM) and how these processes affect the rate of oil biodegradation and ultimate fate of dispersed oil
  - b) Assessment of the degree, rate, and consequences of surfactant leaching from surface slicks and chemically dispersed oil droplets
  - c) Reconciliation of the differences between the empirical evaporation approach and traditional pseudo-component approach
  - d) Quantification of the biodegradation kinetics of dispersed oil
  - e) Improve, verify, and validate oil spill trajectory and fate models
5. Realistic Exposure Regimes/Toxicity Testing.
  - a) Monitoring dispersed oil concentrations at spills of opportunity
  - b) Literature synthesis of dispersed oil toxicity studies
  - c) Standard methods for toxicity testing of dispersed oil appropriate for coastal regimes
6. Integration to Make Short and Long Term Prediction of Effects.
  - a) Synthesis of existing dispersed oil toxicity data to support risk-based decision making for use of dispersants at spills
  - b) Effects of short-term exposure to dispersed oil
  - c) Long-term effects of short-term exposures to dispersed oil
  - d) Integration of fate and toxicity models with population models to predict short- and long-term effects of dispersant application

The current study shows that there are several important data gaps and also several important methodology gaps. The recommended new approaches are:

1. Researchers and studies should employ a new attitude of openness and unbiased views of the topic,
2. The existing literature should be reviewed first. Emphasis should be on peer-reviewed papers. In the oil spill field generally, there is a lot of “re-invention”, both caused by lack of good reviews and by parochialism.
3. Scientists in the correct fields should be employed. Chemists should do chemistry, biologists, biology, and so on.
4. Funding should come from independent sources such as governments.
5. Contractors and consultants, if necessary to be used, should be independent of past biased funding.
6. As much literature as possible should be prepared well and published in peer-reviewed sources.
7. Analytical methods should be consistent with modern, specialized literature in the topic.
8. Study design should include consultation with other experts in the field.
9. Studies should include participation, wherever possible, by others working in the field.
10. Much more work is needed on spills-of-opportunity or other realistic scenarios.
11. Groups with a good record of independent research and high quality output should preferably receive funding.
12. Funding should be re-directed, as much as possible, to new studies. And,
13. Recommendations by the NAS committee and others should be heeded.

Many studies are needed. Emphasis, it is felt, should be placed on the following:

1. Obtaining data sets from real dispersant applications. These data are badly needed for all other fields of research in oil spill dispersion.
2. Much of the emphasis at this point of time should be placed on fundamental studies, such as careful chemical, physical studies, toxicological mechanism studies, etc.
3. Studies on the long-identified gap of measuring the ability of fur and feathers to maintain water-repellency under dispersed oil exposure conditions.
4. Studies on the effects of dispersed oil on a variety of wildlife.
5. Assessment of dispersants, other than Corexit products, on a broad front.
6. Studies of the long-term effects of short-term dispersed oil exposure.
7. Toxicological studies on dispersants and dispersed oil other than acute lethal studies. Studies should follow the many literature trends in the area.
8. Continue sediment-oil interaction studies, however, use of actual sediment at locations and concentrations that are evident at these locations under a variety of environment conditions.
9. Long-term studies on the fate of dispersed oil starting from laboratory going to mesocosms and then ideally to the field.
10. More detailed chemical and physical studies on the interaction of oil and dispersants.



## 6 Detailed Literature Review

### 6.1 Peer-Reviewed Literature

Abdallah, S. Z., Mohamed, and F. M. Ahmed, "Effect of Biological and Chemical Dispersants on Oil Spills", *Petroleum Science and Technology*, Vol. 23: pp. 463–474, 2005.

A study of dispersion and analysis by gas chromatography showed that the lower n-alkanes are much more dispersed than are other components including the larger n-alkanes. This separation was noted for one light Middle-East crude and four different dispersants.

Al-Sabagh, A.M., S.H. El-Hamouly, A.M. Atta, M.R. Noor El-Din and M.M. Gabr, "Synthesis of Some Oil Spill Dispersants Based on Sorbitol Esters and Their Capability to Disperse Crude Oil on Seawater to Alleviate Its Accumulation and Environmental Impact", *Journal of Dispersion Science and Technology*, Vol. 28, pp. 661-670, 2007.

Six mono-, di-, and tri- sorbitol oleate esters [SMO, SDO, and STO corresponding to sorbitol mono-, di-, tri- oleate respectively] were prepared and then ethoxylated using ethylene oxide to obtain six sorbitol esters at different ethylene oxide content (ethylene oxide contents of 5.5, 12, 15, 20, 35, and 45). They were tested as oil spill dispersants individually and in blends. It was found that the blends were more effective than the corresponding individual surfactants. The maximum dispersion capability for the prepared surfactants was obtained at the HLB (hydrophobic-lipophilic balance) range from 9 to 11 for the individual surfactants and blends. The increase of total carbon number in the surfactant alkyl group leads to an increase in dispersion capability of the dispersant. The wide range of ethylene oxide content was used, but the maximum dispersion efficiency was obtained at ethylene oxide =20 in E(20) STO. The dispersion capability increases when the interfacial tension decreases.

Al-Sarawi, H.A., H.M. Mahmoud, and S.S. Radwan, "Pyruvate-utilizing Bacteria as Potential Contributors to the Food Web in the Arabian Gulf", *Marine Biology*, Vol. 154, pp. 373-381, 2008.

Water samples from the Kuwait coast were used for counting and isolating bacteria capable of growth on low molecular weight organic compounds known to be released by picocyanobacteria. The compounds tested were potassium acetate, sodium pyruvate, fumaric acid, succinic acid, sodium citrate and glycerol. For comparison, the bacterial numbers on glucose and Tween 80 and crude oil ( Tween 80 is a surfactant related to those sometimes used in dispersants), as sole sources of carbon and energy were also determined. Sodium pyruvate was, in most cases, the carbon and energy source most commonly utilized by the cultivable surface water bacteria. The most common cultivable bacterial genera on the test carbon sources were *Pseudoalteromonas*, *Vibrio*, *Cobetia* and *Roseobacter*. Less common genera were *Rhodococcus*, *Pseudomonas* and *Bacillus*. Quantification of heterotrophic bacteria associated with cultures of local picocyanobacterial strains, originally isolated from the Gulf surface water, also revealed that the carbon source most commonly utilized by cultivable bacteria was sodium pyruvate. Bacteria were not countable on the oil or Tween, indicating that these were not a preferred source of carbon and would be degraded after sodium pyruvate, if at all.

Atta, A.M., M.E. Abdel-Rauf, N.E. Maysour, A.M. Abdul-Rahiem and A.A. Abdel-Azim, "Surfactants From Recycled Poly (Ethylene Terephthalate) Waste as Water Based Oil Spill Dispersants", *Journal of Polymer Research*, Vol. 13, pp. 39-52, 2006.

Recycled poly (ethylene terephthalate), PET, was modified to produce nonionic surfactants.

Recycling of PET waste was carried out in presence of different weight ratios of diethanolamine and triethanolamine and manganese acetate as catalysts. The molecular weights of the prepared compounds were calculated from hydroxyl number and determined from GPC measurements. The produced oligomers were reacted with polyethylene glycol, PEG, of different molecular weights 400, 1000 and 4000. Interfacial tension and the effectiveness in oil dispersion of the synthesized surfactants using a flask and UV absorption method, were reported. It was found that, the maximum efficiency of oil spill dispersants was reached when the surfactant molecules ended with two PEG 1000 compounds. It is noteworthy that these surfactants are very large compounds compared to surfactants in conventional dispersants.

Barron, M.G., M.G. Carls, J.W. Short and S.D. Rice, "Photoenhanced Toxicity of Aqueous Phase and Chemically Dispersed Weathered Alaska North Slope Crude Oil to Pacific Herring Eggs and Larvae", *Environmental Toxicology and Chemistry*, Vol. 22, pp. 650-660, 2003.

The photoenhanced toxicity of weathered Alaska North Slope crude was tested on the eggs and larvae of Pacific Herring with and without the dispersant, Corexit 9527. The oil alone was toxic to larvae at concentrations below 50 µg/L (approximately equivalent to 50 ppb) total PAH (Polycyclic Aromatic Hydrocarbons). LC<sub>50</sub>s and EC<sub>50</sub>s decreased with time after initial oil exposure. Brief exposure to sunlight of about 2.5 hours/day for 2 days, increased toxicity from 1.5 to 48-fold over control lighting. Photoenhanced toxicity only occurred when oil was present in larval tissue and increased with increasing PAH content in the tissue. Ultraviolet A (UVA) treatments caused a lesser effect than natural sunlight but UVA plus sunlight caused greater toxicity than sunlight alone. The toxicity of chemically-dispersed oil was similar to oil alone in control and UVA treatments, but oil and dispersant treatments were significantly more toxic in the sunlight treatments. The dispersant may be accelerating PAH dissolution into the aqueous phase, resulting in more rapid toxicity. In oil and dispersant exposures, the 96-hour NOEL concentrations in the UVA and sunlight treatment were 0.2 µg/L PAH and 0.01 µg total PAH. Exposure of the eggs to oils and dispersant caused yolk sac edema but UVA treatment did not cause phototoxicity. This confirms the hypothesis that weathered Alaska North Slope oil is phototoxic and that UV is a factor in the mortality of the early life stages of herring exposed to oil and chemically-dispersed oil.

Barron, M.G. and L. Ka'aihue, "Critical Evaluation of CROSERF Test Methods For Oil Dispersant Toxicity Testing Under Subarctic Conditions", *Marine Pollution Bulletin*, Vol. 46, pp. 1191-1199, 2003.

A group of scientists developed protocols known as CROSERF (Chemical Response to Oil Spills: Ecological Research Forum). This paper is a review of these protocols as they relate to subarctic conditions. The CROSERF aquatic testing protocols were developed with the objective of standardizing test methods and reducing inter-laboratory variability. A number of refinements are recommended to adapt the protocols to testing with subarctic species with the expected longer oil persistence. These refinements include: testing fresh and moderately weathered oil under conditions of moderate mixing energy, preparing toxicity test solutions using variable duration of tests from 4 to 7 days, quantifying approximately 40 PAHs and their alkyl homologs, assessing the potential for photoenhanced toxicity and incorporating a bioaccumulation endpoint by measuring tissue concentrations of PAHs. Refinements in the preparation of oil dose solutions, exposure and light regimes and analytical chemistry could increase the utility of the test results for interpreting the toxicity of chemically-dispersed oil in subarctic conditions.

Bhattacharyya, S., P.L. Klerks, and J.A. Nyman, "Toxicity to Freshwater Organisms from Oils and Oil Spill Chemical Treatments in Laboratory Microcosms", *Environmental Pollution*, Vol.122, pp. 205-215, 2003.

Toxicity studies of freshwater-marsh-microcosms containing South Louisiana Crude (SLC) or diesel fuel and treated with a cleaner, Corexit 9580, or dispersant, Corexit 9500, were carried out, using *Chironomus tentans*, *Daphnia pulex*, and *Oryzias latipes*. Bioassays used microcosm water (for *D. pulex* and *O. latipes*) or soil slurry (for *C. tentans*) taken 1, 7, 31, and 186 days after treatment. The crude was less toxic than diesel, chemical additives enhanced oil toxicity, the dispersant was more toxic than the cleaner, and toxicities were greatly reduced by day 186. Toxicities were higher in the bioassay with the benthic species than in those with the two water-column species. A separate experiment showed that *C. tentans*' sensitivity was intermediate to that of *Tubifex tubifex* and *Hyallela azteca*. Freshwater organisms, especially benthic invertebrates, thus appear seriously effected by the toxicants under the worst-case scenario in the test microcosms. The cleaner and dispersant tested were less desirable response options under those conditions.

Bicego, M.C., E. Zanardi-Lamardo, S. Taniguchi and R.R. Weber, "Natural Levels of Dissolved/Dispersed Petroleum Hydrocarbons in the South West Atlantic", *Marine Pollution Bulletin*, Vol. 44, pp. 1152-1169, 2002.

A survey of petroleum hydrocarbons was carried out in the Southwest Atlantic using a spectrofluorimeter with 340 nm excitation and 360 nm for emission. The average values were 0.82 µg/L except near a research station which reached 8.86 µg/L. The values suggest that a typical background for open water in the Southwest Atlantic is 0.3 µg/L.

Bonner, J., C. Page, and C. Fuller, "Meso-scale Testing and Development of Test Procedures to Maintain Mass Balance", *Marine Pollution Bulletin*, Vol. 47, pp. 406-414, 2003.

The Shoreline Environmental Research Facility (SERF, Corpus Christi, Texas) has multiple wave tanks, permitting some control in experimental design of the investigations. This paper outlines the development of a materials balance approach in conducting petroleum experiments at the facility. The first attempt at a materials balance was during a 1998 study on the fate/effects of dispersant use on crude oil. Both water column and beach sediment samples were collected. For the materials balance, the defined environmental compartments for oil accumulation were sediments, water column, and the water surface, while the discharge from the tanks was presumed to be the primary sink. The factors that required development included a need to quantify oil adhesion to the tank surfaces. This was resolved by adhering strips of the polymer tank lining to the tank sides that could be later removed and extracted for oil. A water-surface oil slick quantification protocol was developed, involving the use of solid-phase extraction disks. This protocol was first tested during a shoreline cleaner experiment, and later refined in subsequent dispersant effectiveness studies. The effectiveness tests were designed to simulate shallow embayments which created the need for additional adjustments in the tanks. Since dispersant efficacy is very much affected by hydrodynamics, it was necessary to scale the hydrodynamic conditions of the tanks to those expected in a nearby bay. The use of a scaled model permits the experiment to be reproduced and/or evaluated under different conditions. To minimize wave reflection in the tank, a parabolic wave dissipater was built. In terms of materials balance, this design reduced available surface area as a sink for oil adsorption.

Brandvik, P.J. and L-G. Faksness, "Weathering Processes in Arctic Oil Spills: Meso-Scale Experiments with Different Ice Conditions", *Cold Regions Science and Technology*, Vol. Xx, pp. xxx, 2008.

This paper presents results from a series of meso-scale field experiments performed on Svalbard, Norway, in 2005. The results from these field experiments performed to study oil behavior (evaporation, emulsification, spreading etc.) with different ice conditions (slush ice, 30% and 90% ice coverage) are presented in this paper. Several weathering properties were found to be strongly influenced by the low temperature, reduced oil spreading and wave action caused by increased ice coverage. Reduced water uptake, viscosity, evaporation, and pour point in dense ice conditions extend the operational time window for several contingency methods compared to treatment of oil spills in open waters. For an oil spill in open ice, this could open up for dispersant treatment and in-situ burning even after an extended period of weathering. It should be noted that this dispersant applicability is made on the basis of oil properties and not specific tests.

Bugden, J.B.C., C.W. Yeung, P.E. Kepkay, and K. Lee, "Application of Ultraviolet Fluorometry and Excitation-emission Matrix Spectroscopy (EEMS) to Fingerprint Oil and Chemically Dispersed Oil in Seawater", *Marine Pollution Bulletin*, Vol. 56, pp. 677-685, 2008.

Excitation–emission matrix spectroscopy (EEMS) was used to characterize the ultra violet fluorescence fingerprints of eight crude oils in seawater. When the chemical dispersant Corexit 9500 was mixed with the oils prior to their dispersion in seawater, the fingerprints of each oil changed primarily as an increase in fluorescence over an emission band centered at 445 nm. In order to simplify the amount of information available in the excitation–emission matrix spectra (EEMs), two ratios were calculated. A 66–90% decrease in the slope ratio was observed with the addition of Corexit. When the slope ratios were reduced in complexity to intensity ratios, similar trends were apparent. As a result either of the ratios could be used as a rapid means of monitoring chemically-dispersed oil in the open ocean.

Chandrasekar, S., G.A. Sorial and J.W. Weaver, "Dispersant Effectiveness on Oil Spills: Impact of Salinity", *ICES Journal of Marine Science*, Vol. 63, pp. 1418-1430, 2006.

Salinity effects were investigated using a modified trypsinizing flask termed a baffled flask. Three salinity values in the range 10 to 34 psu (or o/oo) were investigated, representing potential salinity concentrations found in typical estuaries. Three oils were chosen to represent light refined oil, light crude oil, and medium crude oil. Each was tested at three weathering levels to represent maximum, medium, and zero weathering. Two dispersants were chosen for evaluation. A full factorial experiment was conducted for each oil. The interactions between the effects of salinity and three environmental factors, temperature, oil weathering, and mixing energy on dispersion effectiveness were investigated. Each experiment was replicated four times in order to evaluate the accuracy of the test. Statistical analyses of the experimental data were performed for each of the three oils independently for each dispersant treatment (two dispersants and oil controls). A linear regression model representing the main factors (salinity, temperature, oil weathering, flask speed) and second-order interactions among the factors were fitted to the experimental data. Salinity played an important role in determining the significance of temperature and mixing energy on dispersant effectiveness for almost all the oil/dispersant combinations. The impact of salinity at different weathering was only significant for light crude oil with dispersant A.

Chandrasekar, S., G.A. Sorial and J.W. Weaver, "Dispersant Effectiveness on Three Oils Under Various Simulated

Environmental Conditions”, *Environmental Engineering Science*, Vol. 22, pp. 324-336, 2005.

A baffled flask test was used to conduct a series of studies on various factors influencing dispersion. The factors of temperature, oil type, oil weathering, dispersant type and rotation speed were related to the dispersant effectiveness. Three oils were used, Diesel, South Louisiana crude and Prudhoe Bay crude as well as two different dispersants, unidentified. Data analysis shows that for most oils, temperature, mixing energy and weathering were important factors. Empirical relationships between dispersion amount and the variables were developed.

Chapman, H., K. Purnell, R.J. Law and M.F. Kirby, “The Use of Chemical Dispersants to Combat Oil Spills at Sea: A Review of Practice and Research Needs in Europe”, *Marine Pollution Bulletin*, Vol. 54, pp. 827-838, 2007.

A review of the use of dispersants on oil spills that occurred over the 10 year period between 1995 and 2005 has shown that there were relatively few occasions when dispersants were used in response to incidents in European waters. This appears to be chiefly due to unfavorable circumstances for dispersants to work effectively. Of the 77 incidents attended by ITOPF in Europe during the period under review, 6 involved the use of dispersants at sea (8%): one in France, one in Cyprus, two in Greece and two in the UK. Two of the six incidents were spills of heavy fuel oil. A review of policy shows that only Great Britain, of the European countries, considers dispersants to be a primary response tool. Research needs are identified.

Chukwu, L.O. and C.C. Odunzeh, “Relative Toxicity of Spent Lubricant Oil and Detergent against Benthic Macro-invertebrates of a West African Estuarine Lagoon”, *Journal of Environmental Biology*, Vol. 27, pp. 479-484, 2006.

The relative toxicity of spent lubrication oil and detergent, Omo - said to represent a dispersant, were evaluated against the hermit crab, *Clibanarius africanus*, and periwinkle, *Tympanotonus fuscatus*. The detergent toxicity (96-hr  $LC_{50}$  = 5.77 ml/L), was found to be 1.7 times greater than spent engine oil ((96-hr  $LC_{50}$  = 10 ml/L) to the crab, and was 19 times more toxic ((96-hr  $LC_{50}$  = 49 ml/L) than the oil ((96-hr  $LC_{50}$  = 912 ml/L) to the periwinkle.

Cohen, A., M.M. Gagnon and D. Nugegoda, “Biliary PAH Metabolite Elimination in Australian Bass, *Macquaria novemaculeata* Following Exposure to Bass Strait Oil and Chemically Dispersed Crude Oil”, *Bulletin of Environmental Contamination and Toxicology*, Vol. 70, pp. 394-400, 2003.

A study of benzo(a)pyrene type (BaP) and naphthalene-type metabolite elimination in Australian bass, *Macquaria novemaculeata*, after exposure to Bass Strait crude oil and chemically-dispersed crude oil was carried out. Chemically dispersing the crude oil resulted in five times higher concentrations of TPH in the water column, compared to the water soluble fractions alone. There was only a slightly higher amount of the PAH biliary metabolic concentrations after four days in the dispersed samples. This difference disappeared after 12 days depuration and the oil-only had very slightly higher levels. This slight difference was attributed to the fact that the dispersed crude increased metabolic activity and causes a higher degree of sub-lethal stress.

Cohen, A.M., M.M. Gagnon, and D. Nugegoda, “Alterations of Metabolic Enzymes in Australian Bass, *Macquaria novemaculeata*, after Exposure to Petroleum Hydrocarbons”, *Archives of Environmental Contamination and Toxicology*, Vol.49, pp. 200-205, 2005.

Australian bass, *Macquaria novemaculeata*, were exposed to the water-accommodated fractions of Bass Strait crude oil or dispersed crude oil to assess sublethal effects of oil spill remediation techniques on fish. Fish were exposed to these treatments for 16 days either through

the water column or by way of a pre-exposed diet of an amphipod, *Allorchestes compressa*. Fish gills, liver, and white muscle were sampled and cytochrome C oxidase (CCO) and lactate dehydrogenase (LDH) activities quantified. In all treatments fish exposed by way of the water column, aerobic activity increased in the gills, whereas a decrease of this enzymic activity was observed in the liver and white muscle. Exposures by way of the food pathway indicated similar trends. Anaerobic (LDH) activity increased in the gills, liver, and white muscle after waterborne exposures. Stimulation in anaerobic activity also occurred in the liver and white muscle of fish after exposure to contaminated food. CCO activity in the gills was the most sensitive biomarker when monitoring waterborne exposures to petroleum hydrocarbons. In the gills, the dispersed oil treatment resulted in the most pronounced biological response, suggesting that in the short term the use of dispersants on an oil slick might cause the most perturbations to fish metabolism.

Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council of the National Academies), "Introduction", Chapter 1, in *Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C., pp. 9-20, 2006.

This chapter lays the approach to the study and in context to how the study was started. The study notes the context of dispersants within oil spill countermeasures. In general, the use of dispersants might be commended if: (a) an oil slick threatens a sensitive coastal area and mechanical recovery is not feasible, (b) there is sufficient wave energy to break up the surface slick and mix the oil droplets into the water column, c) the oil is of a type known to be dispersible, (d) there is sufficient potential for rapid dilution of the dispersed oil, and (e) in the course of spraying, dispersants are not applied directly to birds or mammals. The report notes that there is insufficient scientific information upon which to make decisions about likely benefits and consequences of dispersant use as an oil spill countermeasure. The report also notes that there is disagreement about how to interpret the results of laboratory, mesocosm and limited field tests to date, because of the difficulty of simulating an adequate range of realistic exposure conditions. The report also notes that there remain basic issues that need to be resolved before dispersants are more fully accepted as a response tool. Examples of these include the sensitivity of effectiveness to environmental factors and oil properties. This change cannot be accurately predicted with sufficient consistency to support decision-making over a variety of conditions. Another example given is that the acute and chronic toxicity of dispersed oil has not been adequately studied under realistic conditions to support decision-making and risk balancing. With respect to near-shore dispersion, it notes that there is a lack of sufficient information regarding effectiveness and potential effects over a wide range of conditions found in nearshore areas, to enable a policy decision on such use.

Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council of the National Academies), "Making Decisions About Dispersant Use", Chapter 2, in *Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C., pp. 21-50, 2006.

Chapter 2 reviews the dispersant decision-making process focusing on USA waters. Three approval processes are in place, case-by-case approval, expedited (or quick) approval and preapproval. In each case, the use of dispersant would require the federal on-scene commander to have approval from the regional response team. Before decisions are made, there are three basic questions: will dispersants work?, can the spill be treated effectively?, and what are the environmental trade-offs? A major consideration in decision-making should be the preparedness

to apply dispersants in adequate quantity. New U.S. Coast Guard rules require the ability to apply dispersants within 12 hours after an oil release within 50 nautical miles of shore. Considerations should also include adequate supply of dispersants and the ability to apply at a dispersant:oil dosage of 1:20. The risk framework includes 3 phases, problem formulation or definition, analysis and risk characterization. The problem definition phases includes: identifying habitats and resources of concern, identifying stressors and response options, and identifying resource interactions. The analysis phase would include: use of a trajectory model to predict what habitats might be impacted, assessment of scientific literature, discussion on estimates and preparation of a risk square, a tool to weight the various risks and options. This analysis should take place before any spill and the information be available to the parties requiring it. Because spill conditions may deviate from the set of scenarios used, real-time decision-making may be necessary. Further information may be necessary to support decision-making: will mechanical response be sufficient?, is the spilled product known to be dispersible?, are sufficient chemical response assets available to treat the spill?, are the environmental conditions conducive to successful application and effectiveness?, and will the effective use of dispersant reduce the impacts of the spill to shoreline and water surface resources without significantly increasing impacts to water column and benthic resources.

Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council of the National Academies), "Dispersant-Oil Interactions and Effectiveness Testing", Chapter 3, in *Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C., pp. 51-134, 2006.

Chapter 3 focuses on dispersant-oil interactions and effectiveness testing. The operative definition of dispersion used here includes movement into the water column and subsurface transport. Discussion on the mechanism of dispersant action and testing efficacy are still topics where there are still major uncertainties and where data gaps exist. The seven requirements for a chemical dispersant to enhance the formation droplets are re-iterated (from the 1989 report): 1) the dispersant must hit the target oil at the desired dosage, 2) the surfactant must have time to penetrate and mix with the oil, 3) the surfactant must orient correctly at the interface, 4) the oil-water interfacial tension should decrease and weaken the cohesive strength of the oil film, 5) sufficient mixing energy must be applied at the oil-water interface to allow the generation of smaller droplets, 6) the droplets must be dispersed throughout the water column by a combination of diffusive and advective forces to minimize droplet collisions and coalescence, and 7) the droplets should then be diluted to non-toxic concentrations and remain suspended in the water column for a long time.

A history of dispersion use was given, noting that dispersants were used seven times in the Gulf of Mexico, however effectiveness was evaluated visually.

Testing is reviewed and it is noted that as the physical scale of the effectiveness increases the cost and realism increase, but the degree to which factors that affect dispersion can be controlled the ability to quantitatively measure effectiveness, decrease. It is noted that when modeling or prediction is carried out, that viscosity is an insufficient predictor of dispersion efficiency. The chemical composition of oil is important and several factors of composition have been shown to correlate well to dispersant effectiveness. Two other factors relating to dispersant effectiveness are the dispersant-to-oil ratio and the oil-to-water ratio, but the most important factor may be the energy applied, energy dissipation rate or mixing energy. In reviewing testing, the Committee notes that there are several important principles of experimental design which are often ignored

including systematic errors which affect the outcome in one direction and random errors. Common systematic errors in dispersant effectiveness measurement included ignoring the evaporation of volatile compounds and incomplete recovery of floating oil. These two errors, as an example given in the report, introduce a positive bias in the estimates of dispersant effectiveness.

Bench scale testing is reviewed and is widely used to evaluate the performance of dispersants and the physical and chemical mechanisms of oil dispersion. A major disadvantage is, of course, that it is difficult to scale the results of these tests to predict performance in the field. Several factors that are difficult to extrapolate include energy regimes, dilution due to horizontal and vertical advection and turbulent diffusion. Bench scale tests are very useful for determining the effectiveness of various dispersant-oil combinations, salinity, temperature effects, effects of oil composition and effects of oil weathering. Recommendations are that energy dissipation rates should be determined over a range of operation conditions, that dispersant effectiveness be measured over a range of energy regimes and that droplet size be measured.

The use of wave tanks to measure effectiveness is also reviewed. The physical characteristics of wave tanks imply that the encounter probability of the dispersant with the oil slick will be higher than can be achieved during a real spill response. Thus, wave-tank tests provide upper limits on operational effectiveness. There is concern that wave-tank tests may also not count for the skinning of oil that often occurs with weathering. Another concern is that the dispersant application system should simulate the droplet-size distributions and impact velocities in real application systems. The wave energies used in tanks should be scalable to actual sea states. It is also noted that coalescence and re-surfacing of dispersed oil droplets occurs and wave-tank experiments should include investigation of these phenomena. A number of wave tanks are portrayed. In summary, it is noted that the advantage of wave tanks is to investigate operational effectiveness components and observe diffusion of droplets more like at sea. The dispersant droplet size generation in tanks may be an important factor. The measurement of effectiveness should also include the measurement of dispersed oil droplet size. The measurement of effectiveness should include the determination of mass balances. It is noted that in tanks where this is attempted, mass balances typically vary from 50 to 75%. It is recommended that mass balance should be attempted in all wave-tank studies of dispersant effectiveness.

Field studies of dispersant effectiveness are reviewed. Field tests can provide opportunities to test and train on full scale equipment as well as to develop and test full scale monitoring equipment and to verify oil fate and transport models. Field tests are however, subject to high costs and legal issues may impede these. A major limitation on field trials is the limited data set that can be obtained from one given trial. The experimental design of field trials is an issue and a primary objective should be to obtain an unbiased estimate of the variation that exists between two experimental slicks. Another major limitation on field trials is the inability to measure remaining oil slick thickness. Sorbent testing is not felt to be an accurate method. Measurement of oil in the water column is also fraught with difficulties, noting that the use of fluorometers only gives one a relative measurement. The output of fluorometers also changes with time, aromatic composition, etc. Visual observation has been used, but a suggestion to improve this is to use 'blind' observers who are not aware of the particular treatment applied. Visual observation is subject to many variables including position of the sun, cloud cover and viewing angle. The results from field trials are generally lower than that obtained in the laboratory suggesting that the



energy regimes in the laboratory are higher than encountered in those field trials. Mass balances should also be attempted on field trials. In conclusion, the complexities and costs of carrying out meaningful field trials suggest that more effort be placed on improving bench-scale and mesocosm research projects. As a recommendation, it is stated that future field-scale work should be based on systematic and coordinated bench-scale and wave-tank testing recommended in this report.

Spills-of-opportunity may provide a good possibility to conduct needed research, and the NAS report notes the following requirements: detailed plans, target areas on the surface need to be identified by smoke bombs or other markers, dispersant to be applied into the wind, good photo and video documentation, water column concentrations measured with fluorometers and grab samples by GCMS, and use of remote sensing techniques. It is also recommended that both dissolved-phase and particulate oil droplets be sampled. Disadvantages of spills-of-opportunity studies include the fact that needed resources are often tied up in response.

Dispersant monitoring after the use can be separated into two categories: information collected to provide information for operational decisions and data gathered for future fate and effect analysis. Fluorometry should primarily be used to locate where to take samples and that samples were taken in the plume. The effluents of the fluorometers should be collected for analysis.

Recommendations overall in this NAS chapter include: a focused set of studies should be developed to enable staff to predict effectiveness of dispersants for different oil types, environmental conditions over time; bench systems should be characterized for energy levels and particle sizes measured; the design of wave-tank studies should specifically test hypotheses regarding operational effectiveness; tank tests to test the recoverability of dispersed oil should be carried out; energy-dissipation tests should be carried out in wave-tanks; a mass balance should be carried out in wave-tanks and coalescence/ re-surfacing studies should be studied in flumes and wave-tanks and more robust monitoring capabilities should be instituted to improve the quality of field data collected during dispersant applications.

Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council of the National Academies), "Transport and Fate", Chapter 4, in *Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C., pp. 135-192, 2006.

This chapter reviews the state-of-the-art knowledge on oil fate and transport, with emphasis on dispersed oil. Several components of behaviour are summarized, including transport, vertical transport, horizontal subsurface transport, and fate and weathering. Fate and weathering includes surface oil evaporation, photooxidation, water-in-oil emulsification, fate of entrained oil droplets in water, dissolution, biodegradation, interaction with suspended particulate material and integration of these factors into oil spill models. Surface transport is important in the physical location of the oil and is primarily influenced by wind, waves and surface currents. Dispersion of a slick, naturally or with the addition of a dispersant, results in the formation of droplets that are entrained into the water column and transported with the subsurface currents. The initial depth of droplet transportation in the vertical plane is taken as proportional to the wave height and many studies show this to be 1.5 times the wave height. Vertical diffusivity can transport droplets deeper into the water column, while buoyancy makes them return to the surface. Vertical diffusivity is thought to range between 1 and 200 cm<sup>2</sup>/s. Droplets obey Stokes' law and rise with a velocity dependent on droplet size. An example is given of droplets 300 and 30 µm in diameter

which would rise at 0.6 cm/s and 0.006 cm/s respectively. The larger droplet would rise 3 m in 8 minutes and the smaller droplet would take about 12 hours. It is noted that much of this knowledge of vertical diffusivity comes from computer models, which are no better than the understanding of the physics which underlies them. Horizontal mixing, on the other hand, consists of two fundamental processes, scale-dependent diffusion and shear dispersion resulting from the combination of velocity gradients in combination with mixing. Some data suggests that horizontal mixing is stronger than vertical mixing, but also horizontal mixing is much less effective, because horizontal plume dimensions are much larger. Three-dimensional models are needed to account for both vertical and horizontal mixing.

Of the fate and weathering components, evaporation is the most important and rapid of weathering processes. Evaporation algorithms are relatively well-developed, however there are differences in approaches to this facet. Some laboratory studies on photooxidation of oil have been carried out and generally point to the creation of increases in the water-soluble fraction consisting of polar compounds. Water-in-oil emulsification has been studied and algorithms developed to make some prediction about the possibility of emulsion formation. True dissolution of individual components from an oil slick is not significant in terms of the overall oil mass balance, however, this is not well understood or modeled. Although the use of chemical dispersants will increase the upper water column concentration of entrained oil droplets and should lead to enhanced dissolution of water-soluble PAH components, no field measurements of this phenomenon have been completed.

The effect of dispersants on biodegradation is a very important topic as one of the stated objectives of using dispersants is to increase biodegradation. The effects of surfactants and oil dispersants on the rate and extent of biodegradation of crude oil and individual hydrocarbons have been extensively investigated for over thirty years with mixed results. In some studies biodegradation is shown to be stimulated, in others there is inhibition and others observed no effects with the addition of dispersants or surfactants. The effect of surfactants and dispersants depends on the chemical characteristics of the dispersants, the hydrocarbons and the microbial community. Other factors such as nutrient concentrations, oil-water ratios and mixing energy also affects the observed biodegradation rate. Many of the studies that observed stimulation may have been confounded by the growth on the dispersants themselves as some of the surfactants are readily biodegradable. The effect of the dispersants on the oil biodegradation rate is most sensitive to the characteristics of the dispersant itself, even if all other factors are kept constant. In one study several specific surfactants were shown to inhibit the biodegradation of classes of hydrocarbons. Only a few surfactants stimulated biodegradation in a culture taken from refinery sludge. Other studies have shown complex interactions of oil, surfactant and conditions. One study showed that the ionic surfactant in Corexit 9527 and 9500 inhibited cultures of alkane-degrading bacteria. The non-ionic surfactants in the same mixture stimulated biodegradation. The variable effects of dispersants and surfactants on oil biodegradation are probably due to their effect on microbial uptake of hydrocarbons. It is clear that surfactants can interfere with attachment of hydrophobic bacteria to oil droplets, making the process very complex to understand. The study concludes that no systematic and reproducible effects of chemical dispersion on the biodegradation rate of crude oil have been demonstrated. The study also notes the experimental systems used to investigate these effects might be inappropriate to represent the environment, because they applied high mixing energy in an enclosed, nutrient sufficient

environment and allowed sufficient time for microbial growth. Microbial growth on open-ocean slicks is likely to be nutrient limited and may be slow relative to processes that lead to the formation of water-in-oil emulsions, which are resistant to biodegradation. It also noted that the most toxic components of the oil, the biodegradation of PAHs, have never been shown to be stimulated by dispersants. The study concludes that only PAH mineralization can be equated with toxicity reduction, stimulation of alkane biodegradation would not be meaningful in the overall toxicity of oil spills.

A review of the current knowledge of oil and suspended particulate material (SPM) is given. It is noted that not much is known about the long-term fate of oil and SPM in the water column. Once formed oil-mineral aggregates appear to be very stable structures and the buoyancy will depend on the oil to mineral ratio. In one study, more oil settled to the bottom in the absence of dispersants than with dispersants. A study also noted that increased clay concentrations were needed to form aggregates as the salinities increased. Dispersant treatment results in greater numbers of oil droplets and thus greater number of interactions with SPM and greater number of agglomerates. The greater number of mineral particles results in larger and more aggregates.

Models which incorporate the fate and transport algorithms are described. It is noted that although more modeling on these complex interactions are needed, that many of the specific fate and behaviour algorithms are poorly understood.

Recommendations on the transport and fate of oil include: coordinated research on bench and wave tank scales to study factors controlling oil dispersion under carefully-controlled, realistic environmental conditions; reconciliation of differences between the empirical evaporation approach and the pseudo-component approaches; coordinated studies of weathering and fate of chemically-dispersed oil with high SPM concentrations present; kinetics of dispersed oil biodegradation should be conducted at low oil-water ratios to simulate conditions at sea; droplet-scale models of biodegradation kinetics should be developed and the needed kinetic parameters developed; biodegradation kinetics and products of high-molecular weight PAHs should be investigated with indigenous seawater microbes; models should be verified and validated using preferably real data. The latter is expanded to include; ability to model physical components of dispersed oil behaviour; ability to model specific components to support toxicity analysis; validate the transport of entrained oil droplets; develop an ability to predict the formation of water-in-oil emulsions under a variety of conditions; and conduct a sensitivity analysis using a 3-d calibrated and advanced model.

Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council of the National Academies), "Toxicological Effects of Dispersants and Dispersed Oil", Chapter 5, in *Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C., pp. 193-275, 2006.

The reports notes several times that there is insufficient understanding of the fate of dispersed oil in aquatic systems, particularly interaction with sediment particles and subsequent effects on the biotic components. The relative importance of different routes of exposure, that is, the uptake and associated toxicity of oil as dissolved components compared to oil droplets and also as mineral particle-associated droplets is poorly understood. Many exposure models and studies do not consider these differences either. The new trends in ecotoxicology, that is population and community-level approaches are gaining wider acceptance in general, and hopefully will be more accepted in the oil spill community in the future.

Testing procedures are also summarized noting that the standard short-term lethal toxicity

test is abundant, but may not be sufficient to assess the potential risk of dispersed oil. These short-term tests are also inadequate to assess potential delayed effects due to oil metabolism, bioaccumulation and photoenhanced toxicity. Some protocols for producing dispersed and chemically-dispersed oil are reviewed. The term, "CEWAF" refers to a standard preparation of chemically-dispersed oil according to a protocol. Toxicity testing using this procedure varies the dose of the solution compared to an alternate procedure of diluting test procedures. Advantages of both procedures are discussed. It is also noted that better exposure quantification is required and testing should move away from 'nominal doses' or simply calculating on the basis of added material. The difference in solubility of the materials can result in orders-of-magnitude errors if using nominal dosage methods. Better testing methods have used TPH or total petroleum hydrocarbons. Advanced methods use and will use quantification by classes such as alkanes, BTEX, and PAHs. Many studies have quantified as many as 50 PAHs in the toxicants.

The 1989 NAS dispersant report concluded that the acute lethal toxicity of chemically-dispersed oil is primarily associated with the dispersed oil and dissolved oil constituents. This report appears to conclude the same. However, several studies are noted in which this conclusion is not valid. Sensitivity to dispersants and dispersants varies significantly by species and life stage. Embryonic and larval stages are more sensitive than adults to both dispersants and dispersed oil. Excellent tables of acute toxicity results are given in this chapter in which these conclusions are shown. In addition to acute toxicity, dispersants may have more subtle effects that influence health of organisms. As an example, dispersants have been reported to affect the uptake of oil constituents. It should be noted, that there is a dearth of longer-term studies on the toxicity of dispersants themselves.

The toxicity of dispersed oil has been examined in a number of studies. As oil consists of many classes of compounds and hundreds of individual compounds, aquatic organisms are potentially exposed to many toxicants with different modes of action and via different exposure routes. The actual toxicity of dispersed oil in the environment depends on many factors: effectiveness of the dispersion, mixing energy, oil type, weathering of the oil, dispersant type, temperature, salinity, exposure duration and light penetration into the water column. In actual practice, some weathering (several hours) would occur after the spill resulting in the loss of many volatiles and enriching the oil in PAHs. PAH toxicity is primal, however several studies have noted that other components in the oil account for much of the toxicity as well. For some organisms, dispersed droplets are also an important route of exposure, either through droplet/gill interactions or through ingestion. Studies show that some organisms accumulate PAHs differently via particulate or dissolved routes. Organisms may also be exposed to oil by contamination of their food. Many oil constituents, such as the monoaromatics and PAHs, are narcotics, that is a substance which causes a state of arrested activity of protoplasmic structures. Some understanding of toxicity modes may come from models such as the toxic unit model. The assumptions currently for these models and the state of knowledge implies that further research is needed.

Several laboratory studies indicate that PAH toxicity increases (from about 12 to about 50,000 times) in exposures conducted with UV light present as it would be in nature, that is in shallow waters. Photo-enhanced toxicity consists of two mechanisms, but the most important one is photosensitization. This occurs when a PAH absorbs energy from the light and then transfers this to dissolved oxygen. This results in enhanced toxicity to many organisms.

The literature reviewed up to the committee's period of writing, indicated that there was no consensus in the relative toxicities of chemically and physically dispersed oil. Many studies found that the PAH concentration is much higher in chemically-dispersed oil than for physically-dispersed oil. Several researchers have recently noted higher toxicities of chemically-dispersed oil, but the interpretation of the committee's report was that these might be less so if calculated only on the basis of PAH concentration. This was true for those studies that used nominal loading calculations and not measured values. Some studies have also noted that the PAH bioaccumulation kinetics are increased in chemical dispersions. Depuration rates were found to either increase or decrease, depending on organism. A useful table of chemically-dispersed and physically-dispersed toxicity is given in the report.

NAS comment on freshwater as well. It was noted that the amount of literature related to effects on freshwater organisms is low. This is attributed to the fact that most common U.S. dispersants have low freshwater efficacy and that the use of dispersants in freshwater is unlikely since most water bodies provide a source of drinking water.

The Committee notes that little is known about the effects of dispersant or dispersed oil on wildlife. The report speculates, that while chemical dispersants may lower the amount of oil to which a bird or aquatic mammal is exposed to, potentially there may be a loss of insulation through reduction of surface tension at the feather/fur-water interface. Since this is a very important factor, more research on this aspect is needed.

Toxicity issues related to microbes have not been well studied and may be confounded by a number of side phenomena, some of which are described in the report.

Coral reefs are noted as being very sensitive to oil or dispersants because the tissue over the skeleton is very thin and because oil droplets adhere to the surface of the organism. Data are currently limited and further studies are recommended.

Recommendations for further studies include: quantifying the weathering and fate of chemically-dispersed oil compared to undispersed oil; obtain data on dissolved-phase PAH and particulate/oil-droplet phase PAH concentrations in test tanks or ideally, at spills-of-opportunity; assess the ability of fur and feathers to maintain water-repellency under dispersed oil exposure conditions; and conduct a series of focused toxicity studies to provide data on photo-enhanced toxicity, estimate the contributions of dissolved and particulate oil phases to toxicity and expand toxicity tests to include delayed effects.

Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council of the National Academies), "Research Priorities to Support Dispersant Use Decision Making", Chapter 6, in *Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C., pp. 277-287, 2006.

This chapter provides overall recommendations for future studies and actions. Many of the specific recommendations appear in the summaries above. The overall recommendations are: field-scale work should be based on coordinated bench-scale and wave-tank testing; conduct a research program to identify the mechanisms and rates of weathering processes that control dispersant effectiveness and include well-coordinated bench scale and wave-tank experiments; conduct a research program to provide data necessary to model chemical, environmental and operational effectiveness of dispersant application including nearshore situations; models should be improved, and validated during experimental spills or during an actual spill; a series of experiments are needed to quantify weathering rates and fate of chemically-dispersed oil droplets compared to undispersed oil; conduct modeling and associated biological assessments with and

without dispersants to develop operation envelopes of dispersant use for oil types, volumes and types of water bodies; conduct focused studies to provide data to predict photo-enhanced toxicity, estimate relative contribution of dissolved and particulate oil phases to representative species toxicity and include an evaluation of delayed effects; ensure that the spill response community is aware of developments in the broad field of ecotoxicology and the various tools developed; and repeating an old recommendation from 1989, conduct studies to assess the ability of fur and feathers to maintain the water-repellency critical for thermal insulation under dispersed oil exposure conditions.

Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council of the National Academies), "Analysis of the Sensitivity of Dispersed Oil Behaviour to Various Processes", Appendix E, in *Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C., pp. 355-377, 2006.

Fourteen model runs were conducted using two different oil spill models to assess the sensitivity and effect of various input parameters on various outputs including fate, trajectory, encounter with a shoreline, etc. The scenarios were found to be instructive, however the need to specify dispersant effectiveness as a model input is the weakest part of the dispersant assessment. Unfortunately, the dispersant effectiveness is one of the most important input parameters. The results of the modeling indicated that without models, it is very difficult to integrate all interacting (and perhaps competing) transport and fate process, oil properties and dispersant use to predict the oil in various compartments and in various areas. It is concluded that transport and fate models should be used to assist in making decisions during an actual spill. This is especially the case in the nearshore where there are even more complex flow fields. Models require improvement and efforts should be made to improve and validate models. This includes undertaking research at laboratory and meso-scale to define the parameters the control oil dispersibility.

Couillard, C.M., K. Lee, B. Legare and T.L. King, "Effect of Dispersant on the Composition of the Water-Accommodated Fraction of Crude Oil and Its Toxicity to Larval Marine Fish", *Environmental Toxicology and Chemistry*, Vol. 24, pp. 1496-1504, 2005.

Newly hatched mummichog, *Fundulus heteroclitus*, were exposed in a 96-h static renewal assay to water-accommodated fractions of dispersed crude oil (DWAF) or crude oil (WAF) to evaluate if dispersant-induced changes in aqueous concentrations of polycyclic aromatic hydrocarbons (PAH) affected larval survival, body length, or ethoxyresorufin-O-deethylase (EROD) activity. Weathered Mesa light crude oil and filtered seawater with or without the addition of Corexit 9500 were used to prepare DWAF and WAF, respectively. At 0.2 g/L, the addition of dispersant caused a two- and fivefold increase in the concentrations of total PAH ( $\Sigma$ PAH) and high-molecular-weight PAH (HMWPAH) with three or more benzene rings. Highest mortality rates (89%) were observed in larvae exposed to DWAF (0.5 g/L;  $\Sigma$ PAH, 479 ng/ml). A reduction in body length was correlated with increased levels of  $\Sigma$ PAH and not with HMWPAH. The EROD activity increased linearly with HMWPAH and not with  $\Sigma$ PAH. Chemical dispersion increased both the  $\Sigma$ PAH concentrations and the proportion of HMWPAH in WAF. Dispersed HMWPAH were bioavailable, as indicated by a significantly increased EROD activity in exposed mummichog larvae. Dispersed oil may represent a significant hazard for larval fish.

Davis, H.K., C.F. Moffat and N.J. Shepherd, "Experimental Tainting of Marine Fish by Three Chemically Dispersed Petroleum Products, With Comparisons to the Braer Oil Spill", *Spill Science and Technology Bulletin*, Vol. 7, pp. 257-278, 2002.

Fish tainting thresholds, and rates of development and loss of taint, were measured using two salmonid and two shell fish species exposed to three chemically-dispersed petroleum products in a study concurrent with the examination of fish affected by the spillage of oil from the wreck of MV Braer. The range of (24 h) tainting thresholds varied from 0.098 to 0.331 mg/l for trout exposed to the three oils, and was no greater than the difference between the values obtained for the diesel oil used in this study and another sample examined previously by the same group. Thresholds were little different for salmon and trout exposed to Forties crude oil but, although the lowest tainting threshold was observed with mussels (0.032 mg/l), crabs appeared to show some resistance to tainting. The rate of induction of oil into fin-fish and mussels produced a readily detectable taint within 6 h of exposure to oil-contaminated water, but rates of uptake, and losses after transfer to clean water, contrasted with the measured fish tainting thresholds for the three different products. Diesel-derived taint persisted for over 10 weeks, much longer than both the medium fuel oil and the Forties crude oil-derived taints, and depuration time increased with oil loading and duration of exposure.

Edwards, K. R., J. E. Lepo and M.A. Lewis, "Toxicity Comparison of Biosurfactants and Synthetic Surfactants Used in Oil Spill Remediation to Two Estuarine Species", *Marine Pollution Bulletin*, Vol. 46, pp. 1309-1316, 2003.

Acute and chronic toxicities of three synthetic surfactants and three microbiologically-produced surfactants were determined and compared in this study for the estuarine epibenthic invertebrate, *Mysidopsis bahia* and the inland silverside, *Menidia beryllina*. The toxicities of the surfactant were determined in standard laboratory static and static-renewal tests of 4–7 d duration. Results were specific to the surfactant, response parameter and test species. The LC<sub>50</sub> values for *M. bahia* ranged from 3.3 mg/l (Triton X-100) to >1000 mg/l (PES-61) and 2.5 mg/l (Triton X-100) to 413.6 mg/l (PES-61) for *M. beryllina*. Chronic first-effect concentrations (mg/l) for the six surfactants ranged from 2.3 to 465.0 (*M. beryllina*) and 1.0 to >1000.0 mg/L (*M. bahia*) based on reductions in growth and fecundity. *M. bahia* was generally the more sensitive species and the toxicities of the biosurfactants were intermediate to those of the synthetic surfactants.

El-Saeed, S.M., R.K. Farag, M.E. Abdul-Raouf, A-A. Abdel-Azim, "Synthesis and Characterization of Novel Crude Oil Dispersants Based on Ethoxylated Schiff Base", *International Journal of Polymeric Materials*, Vol. 57 (9), pp. 860-877, 2008.

A Schiff base prepared from salicylaldehyde and diethylene triamine was ethoxylated by poly (ethylene glycol)(PEG) of different molecular weights, 200, 600, 1000 and 2000, by using b,b-dichlorodiethyl ether as a linking agent. The ethoxylation reaction took place at both ends of the base upon using poly(ethylene glycol) (PEG) 200 and 600, but at one end when PEG 1000 and 2000 were used. The chemical structure of the prepared compounds was confirmed by using IR and proton NMR spectroscopy. Thermodynamic parameters for micellization and adsorption of the prepared compounds were measured based on the surface tension of their solutions at different temperatures. Then, the compounds under investigation were tested as oil spill dispersants by different test methods. It was found that the compounds with lower molecular weights of PEG showed the best dispersant effectiveness.

Fuller, C., J. Bonner, C. Page, A. Ernest, T. McDonald, and S. McDonald, "Comparative Toxicity of Oil, Dispersant and Oil Plus Dispersant to Several Marine Species", *Environmental Toxicology and Chemistry*, Vol. 23, pp. 2941-2949, 2004.

A study was conducted to evaluate the relative toxicity of oil, dispersant or both substances, both on a continuous and a declining concentration over time. Two fish species, *Cyprinodon variegatus* and *Menidia beryllina* and a shrimp, *Americamysis bahia* were used. Microbial toxicity was evaluated using *Vibrio fisheri*. The results suggested that the oil and dispersant mixtures were about the same or less toxicity than the oil mixtures alone. The continuous exposures yielded more toxicity than the declining exposure conditions. Unweathered oil fractions were more toxic than the weathered fractions of the same oil. Toxicity appeared to be largely as a result of the soluble oil components.

Georgiades, E. T., D.A. Holdway, S.E. Brennan, J.S. Butty, and A. Temara, "The Impact of Oil-derived Products on the Behaviour and Biochemistry of the Eleven-armed Asteroid *Coscinasterias muricata* (echinodermata)", *Marine Environmental Research*, Vol. 55, pp. 257-276, 2003.

The study examines the impact of exposure to oil-derived products and results from countermeasures on the behaviour and physiology of the Australian 11-armed asteroid *Coscinasterias muricata*. Asteroids were exposed to dilutions of water-accommodated fraction (WAF) of Bass Strait stabilised crude oil, dispersed oil or burnt oil for 4 days and prey localization behaviour was examined immediately after exposure, and following 2, 7, and 14 days depuration in clean seawater. The prey-localization behaviour of asteroids exposed to WAF and dispersed oil was significantly affected though recovery was apparent following 7 and 14 days depuration, respectively. In contrast, there was no significant change in the prey-localization behaviour of asteroids exposed to burnt oil. Behavioral impacts were correlated with the total petroleum hydrocarbon concentrations (C6–C36) in each exposure solution, WAF (1.8 mg/L), dispersed oil (3.5 mg/L) and burnt oil (1.14 mg/L), respectively. The total microsomal cytochrome P450 content was significantly lower in asteroids exposed to dispersed oil than in any other asteroids, whilst asteroid alkaline phosphatase activity was not significantly affected. This study points out the deleterious impact of dispersed oil to marine organisms.

Gonzalez, J.J., L. Vinas, M.A. Franco, J. Fumega, J.A. Soriano, G. Grueiro, S. Muniategui, P. Lopez-Mahia, D. Prada, J.M. Bayona, R. Alzaga and J. Albaiges, "Spatial and Temporal Distribution of Dissolved/Dispersed Aromatic Hydrocarbons in Seawater in the Area Affected by the Prestige Oil Spill", *Marine Pollution Bulletin*, Vol. 53, pp. 250-259, 2006.

Seawater samples collected at three depths from 68 stations along the Northern Spanish coast were analyzed for dissolved/dispersed petroleum aromatic hydrocarbons by UV-fluorescence and for 25 individual compounds by GC–MS. Sampling was performed in December 2002, just after the Prestige oil spill, and in February–March and September 2003. Higher concentrations of total aromatic hydrocarbons were found at all depths in the samples collected during December 2002 off the Galicia coast, with levels ranging between 0.19 and 28.8 µg/L equivalent oil. These values decreased in the following cruises, until <0.05–2.86 µg/L oil equivalent in September 2003, possibly representing the background levels for the region. However, off the Cantabrian coast they were still high at the surface in the March cruise, probably by the late arrival of the fuel oil to this area. Some coastal hot spots were identified, with values up to 29.2 µg/L fuel-oil equivalent, close to river mouths and urban areas. The individual PAH distributions in the December 2002



sampling off-Galicia were dominated by alkyl-naphthalene derivatives, consistently with the pattern distribution shown by the fuel-oil water accommodated fraction. The higher concentrations were found in the subsurface samples along the Costa da Morte, the area most heavily affected by the spill (average 0.46 µg/L  $\pm$  16 PAHs). The rest of the samples collected in other areas exhibited lower concentrations and a more even distribution of 2–4 ring PAHs, that ranged from 0.09 to 0.37 µg/L (average 0.15 µg/L  $\pm$  16 PAHs), with decreasing trends offshore and down the water column. In September 2003, the values were rather uniform, averaging 0.09 µg/L ( $\pm$  16 PAHs). This paper serves as a good background reference for background hydrocarbons when dispersants were not used.

Greco, G., C. Corra, F. Garaventa, E. Chelossi and M. Faimali, “Standardization of Laboratory Bioassays With *Balanus amphitrite* Larvae For Preliminary Oil Dispersants Toxicological Characterization”, *Chemistry and Ecology*, Vol. 22, pp. S163-S172, 2006.

The aim of this study is to develop bioassays for assessing acute or sublethal responses to oil dispersants using the larval stages of the sessile crustacean *Balanus amphitrite*. The bioassays were standardized using sodium dodecyl sulphate (SDS) as toxic reference compound. Results of acute toxicity (48 h LC50, 7.49 mg/L) and behavioral tests (7 d EC50, 7.79 mg/L) with barnacle larvae showed that their susceptibility to SDS could be comparable with that of *A. bahia* (96 h LC50; 6.6 mg/L). A *B. amphitrite* bioassay is proposed to replace the *A. bahia* bioassay in a standardized toxicological screening of new products for oil-pollution remediation technologies in the Mediterranean Sea.

Guyomarch, J., S. Le Floch and F.-X. Merlin, “Effect of Suspended Mineral Load, Water Salinity and Oil Type on the Size of Oil-Mineral Aggregates in the Presence of Chemical Dispersant”, *Spill Science and Technology*, Vol. 8, pp. 95-100, 2002.

This study investigated the formation of oil–mineral aggregates (OMA) when the oil was chemically-dispersed, focusing on the size distribution of these structures. Results of laboratory experiments show that aggregate size is correlated to the composition of oil and clay, and that for a given concentration of mineral, the average size is near to its maximum size because of the sharp distribution. Other results include the influence of oil type and salinity on the clay concentration corresponding to maximum size. The behavior of a particular oil as OMA depends on the size and buoyancy of its aggregates which will vary with the salinity, suspended mineral load and hydrodynamic conditions.

Haapkylä, J., F. Ramade, and B. Salvat, “Oil Pollution on Coral Reefs: A Review of the State of Knowledge and Management Needs”, *Vie Et Milieu*, Vol. 57, pp. 95-111, 2007.

The effects of oil and oil countermeasures on coral reefs are reviewed. It is concluded that the most suitable clean-up method on shallow fringing reefs and those with high energy, is natural cleanup. Dispersants are not recommended on spills near coral reefs. Toxicity studies reviewed show that coral larvae are very sensitive to dispersants and dispersed oil.

Hamoutene, D., J.W. Payne, A. Rahimtula and K. Lee, “Effect of Water Soluble Fractions of Diesel and an Oil Spill Dispersant (Corexit 9527) on Immune Responses in Mussels”, *Bulletin of Environmental Contamination and Toxicology*, Vol. 72, pp. 1260-1267, 2004.

The short term effects of water-soluble fractions of diesel oil and dispersions of oil using Corexit 9527 were investigated in mussels, *Mytilus* species. Different immune responses were investigated including: number, sensitivity to zymosan particles, ability to adhere to surface and

maintenance of cytoskeleton integrity. Immune responses were investigated in vivo by exposing test animals to the oil or dispersions to establish dose-response relationships or by injecting zymosan particles before and after exposure to the soluble fraction or Corexit dispersions. It was concluded that there was little sensitivity at operational doses of Corexit, but that the dispersant presence sensitized the organisms to zymosan.

Harayama, S., Y. Kasai and A. Hara, "Microbial Communities in Oil-Contaminated Seawater", *Current Opinion in Biotechnology*, Vol. 15, pp.205-214, 2004.

A review of marine biodegradation is presented. It is noted that the vast majority of hydrocarbon-degrading bacteria, including anaerobes, could remain undiscovered, as a large fraction of bacteria inhabiting marine environments are uncultivable. Using culture-independent rRNA approaches, changes in the structure of microbial communities have been analyzed in marine environments contaminated by a real oil spill and in micro- or mesocosms that mimic such environments. *Alcanivorax* and *Cycloclasticus* of the  $\gamma$ -Proteobacteria were identified as two key organisms with major roles in the degradation of petroleum hydrocarbons. *Alcanivorax* is responsible for alkane biodegradation, whereas *Cycloclasticus* degrades various aromatic hydrocarbons.

Hua, J., "Fate of Dispersed Marine Fuel Oil in Sediment Under Pre-Spill Application Strategy", *Ocean Engineering*, Vol. 31, pp. 943-956, 2004.

Models are used to compare the fate of dispersed oil between pre-spill application of dispersant to the oil and post-spill application. This presumes that mixing of the dispersant of the oil in the pre-spill case would be an option. The findings are that much less of the oil in the pre-application situation contacted the sediments than in the post-spill case.

Hua, J., "Biodegradation of Dispersed Marine Fuel Oil in Sediment Under Engineered Pre-Spill Application Strategy", *Ocean Engineering*, Vol. 33, pp. 152-167, 2006.

Biodegradation of marine fuel oil was studied by monitoring changes in residual oil and populations of microorganisms in marine sediments. Biodegradation rates for dispersant and soap water, used as a surrogate for dispersant, were 2.09 and 2.27 g/kg per day, respectively, simulating a pre-application strategy, suggesting that the pre-mixing may promote marine fuel oil dispersion and provide sufficient source of food. This presumes that mixing of the dispersant of the oil in the pre-spill case would be an option. The effect of temperature on the effectiveness of pre-application strategy is particularly obvious for the growth of fungi and *Pseudomonas maltophilia*. The effect of pre-application of soap water on the tolerance of aerobic bacteria, *Escherichia coli*, and *P. maltophilia*, was gradually diminished within 25–33 days.

Kaku, V.J., M.C. Boufadel and A.D. Venosa, "Evaluation of Mixing Energy in Laboratory Flasks Used For Dispersant Effectiveness Testing", *Journal of Environmental Engineering*, Vol. 132, pp. 93-101, 2006.

Two dispersant testing flasks, the swirling flask and the baffled flask, were evaluated for energy using a hot-wire anemometer. These measurements were used to compute the velocity gradient, turbulence microscale and energy dissipation rate per unit mass. The average energy dissipation rates in the swirling flask were about two orders of magnitude smaller than those in the baffled flask. The sizes of the microscales in the baffled flask were much small than that in the swirling flask and approached those thought to be in the sea.

Kaku, V.J., M.C. Boufadel, A.D. Venosa and J. Weaver, "Flow Dynamics in Eccentrically Rotating Flasks Used For Dispersant Effectiveness Testing", *Environmental Fluid Mechanics*, Vol. 6, pp. 385-406, 2006.

Two dispersant testing flasks, the swirling flask and the baffled flask, were evaluated for energy using a hot-wire anemometer. Five rotation speeds of the orbital shaker carrying the flasks were considered,  $\Omega = 50, 100, 150, 175$  and  $200$  rpm. The radial and azimuthal water speeds were measured for each  $\Omega$ . It was found that the flow in the SF is, in general, two-dimensional changing from horizontal at low  $\Omega$  to axi-symmetric at high  $\Omega$ . The flow in the BF appeared to be three-dimensional at all rotation speeds. This indicates that the BF is more suitable for representing the 3-D flow at sea. In the SF, the speeds and energy dissipation rates  $\varepsilon$  increased gradually as the rotation speed increased. Those in the BF increased sharply at rotation speeds greater than 150 rpm. At 200 rpm, the Kolmogorov scale (size of smallest eddies) was about 250 and 50  $\mu\text{m}$  in the SF and BF, respectively

Khan, R.A. and J.F. Payne, "Influence of a Crude Oil Dispersant, Corexit 9527, and Dispersed Oil on Capelin (*Mallotus villosus*), Atlantic Cod (*Gadus morhua*), Longhorn Sculpin (*Myoxocephalus octodecemspinosus*) and Cunner (*Tautoglabrus adspersus*)", *Bulletin of Environmental Contamination and Toxicology*, Vol. 75, pp. 50-56, 2005.

Studies on the influence of dispersant, Corexit 9527, and Dispersed Oil on mature members of Capelin (*Mallotus villosus*), Atlantic Cod (*Gadus morhua*), Longhorn Sculpin (*Myoxocephalus octodecemspinosus*) and Cunner (*Tautoglabrus adspersus*) was carried out. Exposure was for 96 hours. The acute studies showed that mortality was greater in both cod and sculpin exposed to dispersant-WAF mixtures than for any other group. Both the dispersant and the WAF also caused mortality in the cod, but not to the cunner. Examination of gill lesions in the same species showed that epithelial separation and rupture of the secondary lamellae of the gills were observed in fish following exposure to any of the 3 challenges. The percentage of gill lesions was generally greater with the dispersed oil. The authors note that the increase in gill lesions was probably as a result of dispersant-enhanced toxicity.

Kirby, M.F., B.P. Lyons, J. Barry, and R.J. Law, "The Toxicological Impacts of Oil and Chemically Dispersed Oil: UV Mediated Phototoxicity and Implications for Environmental Effects, Statutory Testing and Response Strategies", *Marine Pollution Bulletin*, Vol. 54, pp. 464-488, 2007.

Preliminary testing on the effects of oil on Pacific oyster larvae results show that Kuwait crude oil, both mechanically and chemically dispersed, demonstrates significant levels of photo-enhanced toxicity. The mechanically dispersed oil WAF demonstrated toxic effects at 50% dilution under normal laboratory conditions but effects are evident at concentrations as low as 10% under UV conditions. When dispersed oil was tested, effects were apparent at 25% and 5% dilutions under the room and UV conditions, respectively. Comparisons of the no-observed effect concentrations (NOECs) suggest that UV illumination lowers the concentration of the onset of WAF toxicity of Kuwait crude by up to five times and that with dispersed oil the UV-mediated effects are at a point approximately 10 times lower. The impact of UV-light on WAF toxicity is also borne out by the calculated  $\text{LC}_{50}$ s with the results showing a 2- and 4-fold increase in toxicity with mechanically and chemically dispersed oil, respectively. These preliminary results show that the use of chemical dispersants on oil, not only increases the toxicity of the WAF but can also augment the magnitude of the UV-mediated toxicity.

Kirby, M.F., and R.J. Law, "Oil Spill Treatment Products Approval: The UK Approach and Potential Application to the Gulf Region", *Marine Pollution Bulletin*, Vol. 56, pp. 1243-1247, 2008.

This paper outlines the UK approach to treating agents and how its rationale might be applied to the approval of products specific for the Arabian Gulf region. The United Kingdom has had in place a statutory approval scheme for oil spill treatment products for 30 years. It is based on measures of efficiency and environmental acceptability. Two toxicity tests form an integral part of the assessment, the sea test and the rocky shore test, and work on the premise that approved products will not make the situation significantly worse when added to spilled oil. Issues such as species choice, higher temperatures and salinity and regional environmental conditions are considered.

Klerks, P. L., J.A. Nyman, and S. Bhattacharyya, "Relationship between Hydrocarbon Measurements and Toxicity to a Chironomid, Fish Larva and Daphnid for Oils and Oil Spill Chemical Treatments in Laboratory Freshwater Marsh Microcosms", *Environmental Pollution*, Vol. 129, pp. 345-353, 2004.

This study investigated the extent to which various common hydrocarbon measures can be used to predict toxicity to freshwater aquatic organisms due to fouling by oil. Actual toxicity results, on laboratory freshwater marsh microcosms using two water column species and a benthic species, were studied earlier. The hydrocarbon measures used were TPHg (gravimetric), TPHFID (Flame Ionization Detection), TPHMS (mass spectrometry), TTAH (sum of 41 target aromatic hydrocarbons), principal components of 41 TAHs, and each individual TAH. In general, toxicity was more closely related to TPHMS levels than to TPHFID and TPHg levels. The strongest relationships were found for TTAH levels and for the principal components of the TAHs. Regressions of toxicity on many individual TAHs were also strong, with a single group of compounds explaining as much as 59% of the variation in survival. While the various regressions were highly significant statistically and at times able to accurately predict broad differences in toxicity, the high variation in survival at a specific hydrocarbon concentration indicates that these hydrocarbon measures cannot substitute for actual toxicity determinations in accurately ranking the toxicity of samples from oiled freshwater marshes. The correlations included dispersed crude oil.

Koyama, J. and A. Kakuno, "Toxicity of Heavy Fuel Oil, Dispersant and Oil-Dispersant Mixtures to a Marine Fish, *Pagrus major*", *Fisheries Science*, Vol. 70, pp. 587-594, 2004.

This study examines the toxicity of three dispersants and heavy fuel oil to a marine fish, red sea bream (*Pagrus major*). The 24-h LC<sub>50</sub> of all three dispersants were at least 1500 mg/L; these dispersants appeared relatively less toxic to marine fish than others studied in the past. The mean lethal oil concentration of the water-accommodated oil fraction was 325 mg/L. Mixtures of oil and dispersant were more toxic than dispersant or oil alone. Use of a dispersant-to-oil percentage of 20%, which is recommended by the manufacturer because of its efficiency in oil emulsification and dispersion, yielded higher 24-h oil concentrations and resulted in a higher mortality rate than did the use of higher percentages of dispersant. The application of dispersant to oil in coastal areas, especially with higher activities of fisheries and aquaculture, must be considered carefully in the context of the benefits versus environmental cost.

Lambert, P., "A Literature Review of Portable Fluorescence-based Oil-in-water Monitors", *Journal of Hazardous Materials*, Vol. 102, pp.39-55, 2003.

The results of a literature search review of fluorescence-based portable detectors to measure the real-time concentrations of oil are reported. The focus of this paper has been to summarize the literature about how the instruments were used, including set up and calibration procedures, the

oil and dispersant measured, the approximate concentration range of the oil in the water column, and how the real-time data compared to traditional laboratory techniques.

LaRiviere, D.J., R.L. Autenrieth, and J.S. Bonner, "Redox Dynamics During Recovery of an Oil-impacted Estuarine Wetland", *Water Research*, Vol. 37, pp. 3307-3318, 2003.

Redox potentials and sediment porewater parameters were measured around the periphery of a small cove along the San Jacinto River during a crude oil and chemical dispersant remediation study to distinguish normal dynamics from those caused as a response to stress from oil deposition and chemical treatment and subsequent recovery. Before the application of oil and treatments, sediments displayed average redox potentials of 0–350 mV when not submerged. Within 2 days of the applications, redox potentials in these plots decreased and exhibited a range from 200 to 0 mV for a duration of 5 weeks. Applied treatments significantly reduced the sediments of the wetland. There were not significant differences between the oil-only and oil+dispersant treatments. Reduced redox potentials were indicative of the corresponding sulfate reduction that was also found to be significant following the oil application. GC/MS and MPN analysis indicates this reduction is due to biological oxidation of the crude oil components by alkane- and PAH-degraders in these surficial sediments and validates the usefulness of the redox measurement as an indicator for carbon oxidation. Increases in aqueous phase total organic and inorganic carbon coincided with a decrease in pH shortly after the applications, suggesting incomplete mineralization and the generation of organic acids. While dissolved ferrous iron and sulfide have been found to be good indicators of reductive processes in petroleum-contaminated aquifer sediments in the past; that was not the case in this wetland study. Despite the disappearance of sulfate following the oil application, dissolved ferrous iron and sulfide concentrations remained at pre-application levels suggesting the formation of mackinawite and/or pyrite. The transient exposure of surface sediments to oxygen complicates the consideration of potential solid phase pathways since aqueous iron may be removed by precipitation when oxidized or reduced, making porewater iron a poor indicator for terminal electron accepting processes in wetland sediments.

Lavado, R., G. Janer, and C. Porte, "Steroid Levels and Steroid Metabolism in the Mussel *Mytilus edulis*: The Modulating Effect of Dispersed Crude Oil and Alkylphenols", *Aquatic Toxicology*, Vol. 78S, pp. S65–S72, 2006.

Mussels, *Mytilus edulis*, were exposed to North Sea oil (O) and the mixture of North Sea oil + alkylphenols (OAP), representing the surfactant frequently discharged as a result of production operations, and the effects on tissue steroid levels and steroid metabolism (P450-aromatase and estradiol-sulfotransferase) were monitored. It should be noted that this surfactant is typically used in oil production, not as a dispersant. Levels of free testosterone and free estradiol were much higher in gonad tissue than in peripheral tissue, whereas esterified steroids (released after saponification) were of the same order of magnitude in both tissues. Levels of free steroids determined in gonads were not affected by exposure, but esterified steroids significantly increased in OAP-exposed mussels (up to 2.4-fold). The sulfation of estradiol was investigated as a conjugation pathway, and increased activities were observed in digestive gland cytosol of both O and OAP exposure groups (up to 2.8-fold). Additionally, increased P450-aromatase activity was determined in OAP exposed mussels (up to three-fold, both in gonad and digestive gland), but not in the O group. Altogether, the results indicate that North Sea oil leads to increased sulfation of estradiol, and that in combination with alkylphenols, additional alterations are observed:

increased P450-aromatase, and increased levels of esterified-steroids in gonads. Nonetheless, mussels are able to maintain gonad concentrations of free steroids unaltered, possibly via homeostatic mechanisms such as the conjugation with fatty acid or the formation of sulphate conjugates.

Law, R.J. and C. Kelly, "The Impact of the 'Sea Empress' Oil Spill", *Aquatic Living Resources*, Vol. 17, pp. 389-394, 2004.

In 1996, the tanker, Sea Empress, grounded and released 72,00 tons of a light blend crude oil and 480 tons of heavy fuel oil. The impact of the spill was assessed as much less impact than would be expected from the amount of the oil. Some of the oil moved south and was dispersed and it was estimated that this reduced the amount of oil beaching by 57 to 110 thousand tons.

Li, Z., K., Lee, T. King, M.C. Boufadel, and A.D. Venosa, "Assessment of Chemical Dispersant Effectiveness in a Wave Tank under Regular Non-breaking and Breaking Wave Conditions", *Marine Pollution Bulletin*, Vol. 56, pp. 903-912, 2008.

To achieve assessment of oil dispersant effectiveness under real sea state conditions, a wave tank system was designed to study chemical dispersant effectiveness under controlled mixing energy conditions (regular non-breaking, spilling breaking, and plunging breaking waves). Quantification of oil dispersant effectiveness was based on observed changes in dispersed oil concentrations and oil-droplet size distribution. The study results quantitatively demonstrated that total dispersed oil concentration and breakup kinetics of oil droplets in the water column were strongly dependent on the presence of chemical dispersants and the influence of breaking waves.

Li, Z., P. Kepkay, K. Lee, T. King, M.C. Boufadel and A.D. Venosa, "Effects of Chemical Dispersants and Mineral Fines on Crude Oil Dispersion in a Wave Tank Under Breaking Waves", *Marine Pollution Bulletin*, Vol. 54, pp. 983-993, 2007.

A wave tank study was conducted to investigate the effects of chemical dispersants and mineral fines on the dispersion of oil and the formation of oil-mineral-aggregates (OMAs) in natural seawater. Results of ultraviolet fluorometry and gas chromatography flame ionized detection analysis indicated that dispersants and mineral fines, alone and in combination, enhanced the dispersion of oil into the water column. Measurements taken with a laser in-situ scattering transmissometer showed that the presence of mineral fines increased the total concentration of the suspended particles from 4 to 10  $\mu\text{L/L}$ , whereas the presence of dispersants decreased the particle size (mass mean diameter) of OMAs from 50 to 10  $\mu\text{m}$ . Observation with an epifluorescence microscope indicated that the presence of dispersants, mineral fines, or both in combination significantly increased the number of particles dispersed into the water.

Lindstrom, J.E. and J.F. Braddock, "Biodegradation of Petroleum Hydrocarbons at Low Temperature in the Presence of the Dispersant Corexit 9500", *Marine Pollution Bulletin*, Vol. 44, pp. 739-747, 2002.

This study examined the effects of Corexit 9500 and sediment on microbial mineralization of specific aliphatic and aromatic hydrocarbons found in crude oil. The gross mineralization of crude oil, dispersed crude oil and dispersant by a marine microbial consortium in the absence of sediment was also measured. When provided as carbon sources, the chosen consortium mineralized Corexit 9500 the most rapidly, followed by fresh oil, and finally weathered oil or dispersed oil. However, mineralization in short term assays favored particular components of crude oil (2-methyl-naphthalene > dodecane > phenanthrene > hexadecane > pyrene) and was not affected by addition of nutrients or sediment (high sand, low organic carbon). Adding dispersant

inhibited hexadecane and phenanthrene mineralization but did not affect dodecane and 2-methyl-naphthalene mineralization. Thus, the effect of dispersant on biodegradation of a specific hydrocarbon was not predictable by class. The results were consistent for both high and low oiling experiments and for both fresh and weathered oil. Overall, the results indicate that use of Corexit 9500 could result in either increases or decreases in the toxicity of residual oil through selective microbial mineralization of hydrocarbons.

Liu, B., R.P. Romaine, R.D. Delaune and C.W. Lindau, "Field Investigation on the Toxicity of Alaska North Slope Crude Oil (ANSC) and Dispersed ANSC Crude to Gulf Killifish, Eastern Oyster and White Shrimp", *Chemosphere*, Vol. 62, pp. 520-526, 2006.

A field investigation was conducted on a Louisiana *Spartina alterniflora* shoreline to evaluate the toxic effects of crude oil (Alaska North Slope crude oil, ANS) and dispersed oil (ANS + dispersant Corexit 9500) on three aquatic species indigenous to the Gulf of Mexico: *Fundulus grandis* (Gulf killifish), *Crassostrea virginica* (Eastern oyster), and *Litopenaeus setiferus* (white shrimp). Results indicated that total hydrocarbons concentration value in oiled treatments decreased rapidly in 3 h and were below 1 ppm at 24 h after initial treatment. Corexit 9500 facilitated more ANS fractions to dissolve and disperse into the water column. *L. setiferus* showed short-term sensitivity to the ANS and ANSC + 9500 at 30 ppm. However, most test organisms of each species survived well after 24 h exposure to the treatments. Laboratory tests conducted concurrent with the field investigation indicated that concentrations of crude oil higher than 30 ppm were required for any significant toxic effect on the juvenile organisms tested.

Liu, X. and J.H. Duncan, "An Experimental Study of Surfactant Effects on Spilling Breakers", *Journal of Fluid Mechanics*, Vol. 567, pp. 433-455, 2006.

The dynamics of spilling breakers in the presence of surfactants were studied experimentally. The spilling breakers were produced from Froude-scaled mechanically generated wave packets with average frequencies of 1.15, 1.26 and 1.42 Hz. Separate experiments were performed with the same wave-maker motions in clean water and in water with various bulk concentrations of the soluble surfactants sodium dodecyl sulfate (SDS) and Triton X-100 (TX). These surfactants are similar to those used in dispersants. For nearly all surfactant conditions, the surface-pressure isotherm, equilibrium surface elasticity and surface viscosity were measured in situ in order to characterize the dynamic properties of the free surface. In clean water, all the waves considered in this study, break without overturning of the free surface. This breaking process begins with the formation of a bulge on the forward face of the wave crest and capillary waves upstream of the leading edge of the bulge (called the toe). After a short time, the flow separates under the toe and a turbulent flow is developed while the toe moves rapidly down the wave face. During the toe motion, a train of ripples appears between the toe and the crest and this train of ripples is swept downstream. In the presence of surfactants, the bulge shape is modified and its size generally decreases with increasing surfactant concentration. The capillary waves found upstream of the toe in the clean-water case are dramatically reduced at even the lowest concentrations of surfactants. With surfactants, the start of the breaking process is still initiated when the toe begins to move down the forward face of the wave. The pattern of ripples generated between the toe and the crest of the wave during this phase of the breaking process varies with the concentration of surfactant. Thus with surfactant addition the wave energy from breaking waves is reduced.

Long, S.M. and D.A. Holdway, "Acute Toxicity of Crude and Dispersed Oil to *Octopus pallidus* (Hoyle, 1885) Hatchlings", *Water Research*, Vol. 36, pp. 2769-2776, 2002.

*Octopus pallidus* is a native Australian octopus species found in south-eastern Australia. This experiment investigated the effects of acute exposure to crude and dispersed crude oil and 4-chlorophenol, a reference toxicant, on recently hatched *O. pallidus* by calculating the 48-h LC<sub>50</sub>. Water-accommodated fraction (WAF) of Bass Strait crude oil was prepared using a ratio of one part crude oil to nine parts filtered seawater and mixing for 23 h. Dispersed-WAF was prepared using a ratio of one part Corexit 9527 to 50 parts crude oil and an oil to water ratio of one to nine and mixing for 23 h. The 48 h LC<sub>50</sub> values were 0.39, 1.83 and 0.89 ppm for WAF, dispersed-WAF and 4-chlorophenol, respectively. These results demonstrate that addition of the chemical dispersant Corexit 9527 to WAF does not increase the toxicity of WAF to *O. pallidus* hatchlings.

Ma, X., A. Cogswell, Z. Li and K. Lee, "Particle Size Analysis of Dispersed Oil and Oil-Mineral Aggregates with an Automated Ultraviolet Epi-Fluorescence Microscopy System", *Environmental Technology*, Vol. 29, pp. 739-748, 2008.

This paper describes microscopic analysis for quantitative measurement of oil droplets. Integration of a microscope with bright-field and ultraviolet epi-fluorescence illumination (excitation wavelengths 340–380 nm; emission wavelengths 400–430 nm) fitted with a computer-controlled motorized stage, a high resolution digital camera, and image-analysis software, enables automatic acquisition of multiple images and facilitates efficient counting and sizing of oil droplets. Laboratory experiments were conducted with this system to investigate the size distribution of chemically-dispersed oil droplets and oil-mineral aggregates in baffled flasks that have been developed for testing chemical dispersant effectiveness. Image acquisition and data processing methods were developed to illustrate the size distribution of chemically dispersed oil droplets, as a function of energy dissipation rate in the baffled flasks, and the time-dependent change of the morphology and size distribution of oil-mineral aggregates. As a quantitative analytical tool, epifluorescence microscopy shows promise for application in research on oil spill response technologies, such as evaluating the effectiveness of chemical dispersant and characterizing the natural interaction between oil and mineral fines.

MacNaughton, S.J., R. Swannell, F. Daniel and L. Bristow, "Biodegradation of Dispersed Forties Crude and Alaskan North Slope Oils in Microcosms Under Simulated Marine Conditions", *Spill Science and Technology Bulletin*, Vol. 8, pp. 179-186, 2003.

A study of the comparative degradation of crude oils, with and without dispersant was carried out as two separate experiments. In one experiment Forties crude was mixed with a dispersant, Corexit 9500, and nutrients and incubated for 27 days at 15°C. In another, experiment Alaska North Slope, treated similarly, was incubated at 8°C for 35 days. All results were compared to a 'killed' control with no nutrients added. A third test was carried out in which only seawater was added and no dispersant. The test vessel was similar to the Mackay dispersant apparatus with a high air flow. One test was run for each trial. Observations of colonies forming, particles and visual were recorded. The amount of total alkanes was measured in the samples. In both studies microbial colonies started after 4 days as well as the formation of neutrally-buoyant clusters consisting of oil, bacteria, protozoa and nematodes. By day 16, the sizes of the clusters increased and sank to the bottom of the test flask. In the 'killed' controls, no bacteria were observed. The TPH measurements in all three tests showed similar end results, with the dispersant



one being slightly lower in the Forties case, but not in the Alaska oil case. Discussion focused on why no biodegradation was observed in the Alaska oil case but was observed in the Forties oil case.

Martin-Skilton, R., R. Thibaut, and C. Porte, "Endocrine Alteration in Juvenile Cod and Turbot Exposed to Dispersed Crude Oil and Alkylphenols", *Aquatic Toxicology*, Vol. 78S, pp.S57–S64, 2006.

Juvenile Atlantic cod (*Gadus morhua*) and turbot (*Scophthalmus maximus*) were exposed for 3 weeks in a continuous water flow to 0.5 ppm of dispersed North Sea crude oil, 0.5 ppm of dispersed North Sea crude oil spiked with 0.1 ppm of a mixture of alkylphenols (surfactants used in offshore oil production - similar to surfactants once used as dispersants), and 30 ppb of nonylphenol (NP). As potential markers of endocrine alteration, key enzymatic activities involved in both synthesis (17 $\beta$ -hydroxysteroid dehydrogenases and P450 aromatase) and metabolism (liver UDP-glucuronosyltransferases (UGT) and sulfotransferases) of steroids were assessed together with circulating levels of testosterone and estradiol in plasma. NP-exposed turbot had lower ovarian P450 aromatase, lower levels of testosterone and estradiol in plasma, and lower glucuronidation rates of sex steroids than those from the control group. In contrast, higher liver UGT-testosterone, and a trend towards higher P450 aromatase was detected in oil-exposed specimens. Those exposed to the combination oil + alkylphenols had lower levels of estradiol in plasma than controls, and no significant effects on any the enzymatic activities tested was observed. All these alterations were more evident in turbot than in cod. In fact, apart from a higher glucuronidation rate of estradiol detected in the liver of NP-exposed cod, no significant differences were observed between control and exposed cod. To the turbot, the addition of the surfactants caused marked toxicity.

Mielbrecht, E.E., M.F. Wolfe, R.S. Tjeerdema and M.L. Sowby, "Influence of a Dispersant on the Bioaccumulation of Phenanthrene by Topsmelt (*Atherinops affinis*)", *Ecotoxicology and Environmental Safety*, Vol. 61, pp. 44-52, 2005.

This study investigated the influence of a chemical dispersant on the uptake, biotransformation, and depuration of a model hydrocarbon, [<sup>14</sup>C]-phenanthrene ([<sup>14</sup>C]PHN), by larval topsmelt, *Atherinops affinis*. Exposure was via aqueous-only or combined dietary and aqueous routes from a water-accommodated fraction (WAF) of Prudhoe Bay Crude Oil or a WAF of Corexit 9527-dispersed PBCO (DO). Trophic transfer was measured by incorporating into exposure media both a rotifer, *Brachionus plicatilis*, as food for the fish and a phytoplankton, *Isochrysis galbana*, as food for the rotifers. Short-term (<4 h) bioconcentration of PHN was significantly decreased in topsmelt when oil was treated with dispersant, but differences diminished after 12 hours. When trophic transfer was incorporated, PHN accumulation was initially delayed but after 12 h attained similar levels. Dispersant use also significantly decreased the proportion of biotransformed PHN (as 9-phenanthrylsulfate) produced by topsmelt. However, overall PHN depuration was not affected by dispersant use. Thus, chemical dispersant use in oil spill response may reduce short-term uptake but not long-term accumulation of hydrocarbons such as PHN in pelagic fish.

Moles, A., L. Holland and J. Short, "Effectiveness in the Laboratory of Corexit 9527 and 9500 in Dispersing Fresh, Weathered and Emulsion of Alaska North Slope Crude Oil Under Subarctic Conditions", *Spill Science and Technology Bulletin*, Vol. 7, pp. 241-247, 2002.

The effect of various amounts of weathering (no weathering, 20% evaporatively weathered,

and emulsification) on the effectiveness of oil dispersants Corexit 9527 and 9500 in dispersing Alaska North Slope crude oil into the water column was tested under laboratory conditions at a combination of salinities and temperatures. A modified version of the swirling flask effectiveness test was used at temperatures of 3, 10 and 22°C with salinities of 22o/oo and 32o/oo. Petroleum dispersed into the water column following application of dispersant was measured by gas chromatography with flame ionization detection. Based on comparison of unresolved complex mixtures, dispersants dispersed less than 40% of the fresh oil and less than 10% of the weathered oil and were most effective (25–75%) when used to disperse a stable oil/water emulsion at 10°C. At the combinations of temperature and salinity most common in the estuaries and marine waters of Alaska, dispersant effectiveness was less than 10%, the detection limits of the tests. The results indicate that oil weathering state, seawater salinity and temperature are important factors affecting dispersant performance.

Nichols, W. J., “An Overview of the USEPA National Oil and Hazardous Substances Pollution Contingency Plan, Subpart J Product Schedule (40 CFR 300.900)”, *Spill Science and Technology Bulletin*, Vol. 8, pp. 521-527, 2003.

This paper is an overview of the United States approval and testing requirements for oil spill treating agents. Some perspectives on dispersant and research are also given.

Nyman, J.A., P.L. Klerks, and S. Bhattacharyya, “Effects of Chemical Additives on Hydrocarbon Disappearance and Biodegradation in Freshwater Marsh Microcosms”, *Environmental Pollution*, Vol. 149, pp. 227-238, 2007.

Microcosms were set up to measure the effects of chemical additives on hydrocarbon fate in freshwater marshes. The test microcosms received no hydrocarbons, South Louisiana crude, or diesel; and no additive, a dispersant, or a cleaner. Oil fate was determined the concentration of four total petroleum hydrocarbon (TPH) measures and 43 target hydrocarbons in water and sediment fractions 1, 7, 31, and 186 days later. Disappearance was distinguished from biodegradation via hopane-normalization. After 186 days, TPH disappearance ranged from 24% to 97%. There was poor correlation among the four TPH measures, which indicated that each quantified a different suite of hydrocarbons. Hydrocarbon disappearance and biodegradation were unaltered by these additives under worse-case scenarios. There was generally no benefit in increased biodegradation nor a significant decline in degradation. The authors however conclude that use of these additives must generate benefits that outweigh the lack of effect on biodegradation demonstrated in this report, and the increase in toxicity that they reported earlier.

Otitoloju, A.A., “Crude Oil Plus Dispersant: Always a Boon or Bane?”, *Ecotoxicology and Environmental Safety*, Vol. 60, pp. 198-202, 2005.

The toxicities of a Nigerian crude oil, Forcados Light, a dispersant, Biosolve, and their mixtures, based on ratios 9:1, 6:1 and 4:1 (v/v), were evaluated against the juvenile stage of prawn, *Macrobrachium vollehovenii*, in laboratory bioassays. On the basis of the derived toxicity indices, crude oil with 96-h LC<sub>50</sub> value of 0.28 ml/L was found to be about six times more toxic than the dispersant (96-h LC<sub>50</sub> 1.9 ml/L) when acting alone against *M. vollehovenii*. Toxicity evaluations of the mixtures of crude oil and dispersant revealed that effects of the crude oil/dispersant mixtures varied, depending largely upon the proportion of addition of the mixture components. The interactions between mixture of crude oil and dispersant at the test ratios of 9:1 and 4:1 were found to conform with the model of synergism, while the interactions between the mixture prepared based on ratio 6:1 conformed with the model of antagonism, based on the concentration addition model. Furthermore, the mixtures prepared based on ratios 9:1 and 6:1

were found to be less toxic than crude oil when acting singly against *M. vollenhovenii* while the mixture prepared based on ratio 4:1 was found to have similar toxicity with crude oil when acting singly, based on the derived synergistic ratio values.

Page, C.A., J.S. Bonner, T.J. McDonald and R.L. Autenrieth, "Behaviour of a Chemically Dispersed Oil in a Wetland Environment", *Water Research*, Vol. 36, pp. 3821-3833, 2002.

An experiment was conducted at a wetland research facility, to investigate the behavior and effects of chemically dispersed oil (CDO) using Corexit 9500. The replicated treatments included oiled control, high-dose CDO (1:10 dispersant-to-oil ratio (DOR)), low-dose CDO (1:20 DOR), as well as an unoiled control. Known amounts of oil or dispersed oil were added to the respective plots. Sediment samples were taken over a 99-day period using a 5-cm-diameter coring device. The GCMS results for both total target saturate hydrocarbons and total target aromatic hydrocarbons were measured and data were modeled using nonlinear regression. The overall (including abiotic and biotic) petroleum loss rates for the dispersed-oil treatments were not statistically different when compared to the oiled control. However, the initial concentrations for the dispersed-oil treatments were statically lower than for the oiled control. From this, it can be inferred that the dispersed oil was more prone to flush off the sediments, as was visually observed. Biodegradation rates were also determined for all treatments; it was concluded that there were no differences when comparing each dispersed-oil treatment to the oiled control. The sediments from each plot were also analyzed for microbial population numbers and acute toxicity (Microtox 100% Test). Statistical analyses for both sets of data found no significant differences for the dispersed-oil treatments when compared to the oiled control.

Perkins, R.A., S. Rhoton and C. Behr-Andres, "Comparative Marine Toxicity Testing: A Cold-Water Species and Standard Warm-Water Test Species Exposed to Crude Oil and Dispersant", *Cold Regions Science and Technology*, Vol. 42, pp. 226-236, 2005.

This paper reports the toxicity testing of oil and dispersed oil to a cold-water species, Tanner crab (*Chionocetes bairdi*) larvae, and compares the result to two standard warm-water test species, the saltwater mysid (*Mysidopsis bahia*) and fish (*Menidia beryllina*) larvae. The method of reporting the exposure dose: loading rate, volatile organic analytes (VOA, C6–C9), total petroleum hydrocarbons (TPH C10–C36), or their summation, total hydrocarbon concentrations (THC C6–C36) would result in different conclusions. These differences are especially important with the water-accommodated fraction (WAF) in cold water, but may as well be significant when reporting the chemically enhanced-water accommodated fraction (CE-WAF), dispersed oil. The differences are chiefly due to the greater accommodation of VOA in the colder water.

Pollino, C.A. and D.A. Holdway, "Reproductive Potential of Crimson-Spotted Rainbowfish (*Melanotaenia fluviatilis*) Following Short-Term Exposure to Bass Strait Crude Oil and Dispersed Crude Oil", *Environmental Toxicology*, Vol. 17, pp. 138-145, 2002.

The short-term effects of a water-accommodated fraction of crude oil (WAF) and a dispersed crude oil water-accommodated fraction (DCWAF) on selected reproductive end points were measured by conducting 3-day exposures to the crimson-spotted Rainbowfish, *Melanotaenia fluviatilis*. Exposures were followed by 14-day depuration periods to determine the ability of fish to recover from the exposure. There were no changes to egg production, hatchability, or larval lengths for the WAF and DCWAF test periods. There were no changes to plasma estradiol or

testosterone concentrations, gonadosomatic indices, or histopathological organization of gonad tissues after the exposure and depuration periods for both WAF and DCWAF. As reproductive parameters were not altered after 3 days of exposure and 14 days of depuration, crimson-spotted Rainbowfish were able to endure short-term exposures to crude oil and dispersed crude oil.

Radwan, S.S., R.H. Al-Hasan, N. Ali, S. Salamah and M. Khanafer, "Oil-consuming Microbial Consortia Floating in the Arabian Gulf", *International Biodeterioration and Biodegradation*, Vol. 56, pp.28-33, 2005.

Picocyanobacteria floating on the Arabian Gulf were found associated with heterotrophic bacteria. Haemocytometer counting of fresh 1-cm surface water revealed 107–108 bacterial cells ml/L, but only 102–103 cells ml/L in 10-cm deep water samples. The heterotrophic bacteria comprised hydrocarbon utilizers that could grow on a mineral medium containing crude oil as sole carbon and energy source. Growth and hydrocarbon consumption potential of individual types of oil-utilizing bacteria in culture were higher in the presence of the picocyanobacteria than in their absence. Evidence was presented that picocyanobacterial cells may accumulate hydrocarbons from the medium, and subsequently make those compounds available to the associated hydrocarbon-utilizing bacteria. It was concluded that this microbial consortium, which is apparently of cosmopolitan occurrence, could be active in controlling marine oil-pollution.

Ramachandran, S.D., P.V. Hodson, C.W. Khan and K. Lee, "Oil Dispersant Increases PAH Uptake by Fish Exposed to Crude Oil", *Ecotoxicology and Environmental Safety*, Vol. 59, pp. 300-308, 2004.

This paper reports on an experiment to measure whether oil dispersion increases or decreases the exposure of aquatic species to the toxic components of oil. To evaluate whether fish would be exposed to more polycyclic aromatic hydrocarbon (PAH) in dispersed oil relative to equivalent amounts of the water-accommodated fraction (WAF), measurements were made of CYP1A induction in trout exposed to the dispersant, Corexit 9500, WAFs, and the chemically enhanced WAF (CEWAF) of three crude oils. The crude oils comprised the higher viscosity Mesa and Terra Nova and the less viscous Scotian Light. Total petroleum hydrocarbon and PAH concentrations in the test media were determined to relate the observed CYP1A induction in trout to dissolved fractions of the crude oil. CYP1A induction was 6- to 1100-fold higher in CEWAF treatments than in WAF treatments, with Terra Nova having the greatest increase, followed by Mesa and Scotian Light. Mesa had the highest induction potential with the lowest EC<sub>50</sub> values for both WAF and CEWAF. The dispersant Corexit was not an inducer and it did not appear to affect the permeability of the gill surface to known inducers such as  $\beta$ -naphthoflavone. These experiments suggest that the use of oil dispersants will increase the exposure of fish to hydrocarbons in crude oil.

Ramachandran, S.D., M.J. Swezey, P.V. Hodson, M. Boudreau, S.C. Courtney, K. Lee, T. King and J.A. Dixon, "Influence of Salinity and Fish Species on PAH Uptake From Dispersed Crude Oil", *Marine Pollution Bulletin*, Vol. 52, pp. 1182-1189, 2006.

The induction of CYP1A enzymes of fish was measured to test the effect of salinity on PAH availability. Freshwater rainbow trout and euryhaline mummichog were exposed to water accommodated fractions (WAF), and chemically-enhanced water accommodated fractions (CEWAF) at 0 o/oo, 15 o/oo, and 30 o/oo salinity. For both species, PAH exposure decreased as salinity increased whereas dispersant effectiveness decreased only at the highest salinity. Risks to fish of PAH from dispersed oil are concluded to be the greatest in coastal waters where salinities are low. The use of chemical oil dispersants to minimize spill impacts causes a transient

increase in hydrocarbon concentrations in water, which increases the risk to aquatic species if toxic components become more bioavailable. The risk of effects depends on the extent to which dispersants enhance the exposure to toxic components, such as polycyclic aromatic hydrocarbons (PAH). Increased salinities can reduce the solubility of PAH and the efficiency of oil dispersants.

Reed, M., P. Daling, A. Lewis, M.K. Ditlevsen, B. Brørs, J. Clark, and D. Aurand, "Modelling of Dispersant Application to Oil Spills in Shallow Coastal Waters" *Environmental Modelling and Software*, Vol. 19, pp. 681-690, 2004.

Coupled three-dimensional oil spill and hydrodynamic models were used to assist in the design of an experiment in Matagorda Bay, on the Texas coast. The purpose of the modeling work was to map hydrocarbon concentration contours in the water column and on the seafloor as a function of time following dispersant application.

Saeki, H., M. Saskaki, K. Komatsu, A. Miura and H. Matsuda, "Oil Spill Remediation by Using the Remediation Agent JE 1058BS that Contains a Biosurfactant Produced by *Gordonia* sp. Strain Je-1058, *Bioresource Technology* Vol. xx, pp. xxx, 2008. (In press)

A remediation agent containing a biosurfactant was prepared by spray drying the sterilized culture broth of *Gordonia* sp. strain JE-1058. When tested in the baffled flask test showed a strong potential to be applied as an oil spill dispersant even in the absence of a solvent. It also proved to be an effective bioremediation agent. The addition of JE1058BS to seawater stimulated the degradation of weathered crude oil (ANS). Its addition also stimulated the removal of crude oil from the surface of contaminated sea sand.

Scarlett, A., T.S. Galloway, M. Canty, E.L. Smith and J. Nilsson, "Comparative Toxicity of Two Oil Dispersants, Superdispersant-25 and Corexit 9527, to a Range of Coastal Species", *Environmental Toxicology and Chemistry*, Vol. 24, pp. 1219-1227, 2005.

This study compares the toxicity of the two dispersants, Corexit 9527 and Superdispersant-25 (SD-25), to a range of marine species representing different phyla occupying a wide range of niches: The marine sediment-dwelling amphipod *Corophium volutator* (Pallas), the common mussel, *Mytilus edulis*, the symbiotic snakelocks anemone, *Anemonia viridis*, and the seagrass *Zostera marina*. Organisms were exposed to static dispersant concentrations for 48-h and median lethal concentration ( $LC_{50}$ ), median effect concentration ( $EC_{50}$ ), and lowest-observable-effect concentration (LOEC) values obtained. The sublethal effects of 48-h exposures and the ability of species to recover for up to 72 h after exposure were quantified relative to the 48-h endpoints. Results indicated that the anemone lethality test was the most sensitive with LOECs of 20 ppm followed by mussel feeding rate, seagrass photosynthetic index and amphipod lethality, with mussel lethality being the least sensitive with LOECs of 250 ppm for both dispersants. The results were consistent with the hypothesis that dispersants act physically and irreversibly on the respiratory organs and reversibly, depending on exposure time, on the nervous system. Superdispersant-25 was found overall to be less toxic than Corexit 9527 and its sublethal effects more likely to be reversible following short-term exposure.

Shafir, S., J. Van Rijn, and B. Rinkevich, "Short and Long Term Toxicity of Crude Oil and Oil Dispersants to Two Representative Coral Species", *Environmental Science and Technology*, Vol. 41, pp. 5571-5574, 2007.

This study employed a nubbin assay on more than 10,000 coral fragments to evaluate the short- and long-term impacts of dispersed oil fractions (DOFs) from six commercial dispersants,

the dispersants and water-soluble-fractions (WSFs) of Egyptian crude oil, on two Indo Pacific branching coral species, *Stylophora pistillata* and *Pocillopora damicornis*. Survivor status and growth of nubbins were recorded for up to 50 days following a single, short (24 hour) exposure to toxicants in various concentrations. Manufacturer-recommended dispersant concentrations proved to be highly toxic and resulted in mortality for all nubbins. The dispersed oil and the dispersants were significantly more toxic than crude oil WSFs. As corals are particularly susceptible to oil detergents and dispersed oil, the results of these assays rules out the use of any oil dispersant in coral reefs and in their vicinity. The ecotoxicological impacts of the various dispersants on the corals could be rated on a scale from the least to the most harmful agent, as follows: Slickgone > Petrotech > Inipol > Biorieco > Emulgal > Dispolen.

Sorial, G.A., A.D. Venosa, K.M. Koran, E. Holder and D.W. King, "Oil Spill Dispersant Effectiveness Protocol: I.Impact of Operational Variables", *Journal of Environmental Engineering*, Vol. 130, pp. 1073-1084, 2004.

A baffled flask test was used to conduct a series of studies on various factors influencing dispersion. The factors or temperature, oil type, oil weathering, dispersant type and rotation speed were related to the dispersant effectiveness. Variances included examining 3 analytical protocols. Data analysis shows that the baffled flask provided the least error coefficient.

Sorial, G.A., A.D. Venosa, K.M. Koran, E. Holder and D.W. King, "Oil Spill Dispersant Effectiveness Protocol: II.Performance of Revised Protocol", *Journal of Environmental Engineering*, Vol. 130, pp. 1085-1093, 2004.

A baffled flask test was used to conduct a series of studies on various factors influencing dispersion and error between different protocols. Variances included examining the coefficient of variation for various tests. Data analysis shows that the baffled flask provided the least error.

Srinivasan, R., Q. Lu, G.A. Sorial, A.D. Venosa and J. Mullin, "Dispersant Effectiveness of Heavy Fuel Oils Using the Baffled Flask Test", *Environmental Engineering Science*, Vol. 24, pp. 1307-1320, 2007.

The baffled flask protocol was used to determine the effectiveness of three dispersants on two heavy fuel oils, namely IFO 180 and IFO 380. The dispersants tested were Corexit 9500, Superdispersant 25, and Agma Superconcentrate DR379. A factorial experimental design was conducted to study the effect of different variables. The factors and levels of each test variable were three dispersant to oil ratios (DOR) (1:100, 2:100, and 4:100), two temperatures (16°C and 5°C), and three flask rotation speeds (150, 200, and 250 rpm). The percent effectiveness encountered ranged from less than 5% for untreated IFO oils to around 80% for one IFO and one dispersant at high mixing at 16°C. In general, dispersion effectiveness increased with increased temperature, DOR, and mixing rate. Statistical analysis was performed on the experimental data to determine the significant factors. Mixing speed was found to be a significant factor in all the oil:dispersant combinations and DOR in all tests involving two of the dispersants. The effect of temperature was observed for all combinations involving IFO 180 and a few involving IFO 380, and a significant two-way interaction was observed between temperature and the other two factors in almost all the cases. The experimental data were also compared with results from other laboratory and wave-tank dispersant effectiveness studies conducted on the two IFO oils. For both IFO 180 and IFO 380, the results compared well with the various laboratory and wave-tank tests.

Sterling, Jr., M.C., J.S. Bonner, A.N.S. Ernest, C.A. Page and R.L. Autenrieth, "Chemical Dispersant Effectiveness Testing: Influence of Droplet Coalescence", *Marine Pollution Bulletin*, Vol. 48, pp. 969-977, 2004.

Thermodynamic and kinetic investigations were performed to determine the influence of coalescence of chemically dispersed crude oil droplets in saline waters. For the range of pH (4–10) and salinity (10‰, 30‰, 50‰) values studied,  $\zeta$ -potential values ranged from -3 to -10 mV. As the interaction potential values calculated using Derjaguin–Landau–Verwey–Overbeek (DLVO) theory were negative, the electrostatic barrier did not produce significant resistance to droplet coalescence. Coalescence kinetics of premixed crude oil and chemical dispersant were determined within a range of mean shear rates ( $\text{Gm}^{-1/4}$ , 5, 10, 15, 20  $\text{s}^{-1}$ ) and salinity (10‰, 30‰) values. Coalescence reaction rates were modeled using Smoluchowski reaction kinetics. Measured collision efficiency values ( $\alpha = 0.25$ ) suggest insignificant resistance to coalescence in shear systems. Experimentally determined dispersant efficiencies were 10–50% lower than that predicted using a non-interacting droplet model ( $\alpha = 0.0$ ). Unlike other protocols in which the crude oil and dispersant are not premixed, salinity effects were not significant in this protocol. This approach allowed the effects of dispersant–oil contact efficiency ( $\eta_{\text{contact}}$ ) to be separated from those of water column transport efficiency ( $\eta_{\text{transport}}$ ) and coalescence efficiency ( $\eta_{\text{coalescence}}$ ).

Tkalich, P., “A CFD Solution of Oil Spill Problems”, *Environmental Modelling and Software*, Vol. 21, pp. 271–282, 2006.

The Multiphase Oil Spill Model is a model using recent developments in areas of Computational Fluid Dynamics (CFD) and environmental modelling. A consistent Eulerian approach is applied across the model, the slick thickness is computed using layer-averaged Navier–Stokes equations, and the advection–diffusion equation is employed to simulate oil dynamics in the water column. To match the observed balance between advection, diffusion and spreading phenomena, a high-order accuracy numerical scheme is developed. Vertical dynamics of oil droplets plays a major role in oil mass exchange between the slick and the water column. Oil mixing by breaking waves is parameterised using newly developed kinetic equations. Majority parameters of oil, water column and breaking waves are conveniently combined into a single mixing factor, quantifying the partitioning of oil between the slick and the water column. The model is able to predict rates of oil entrainment for different scenarios of dispersant application with respect to the storm intensity and duration. Governing equations are verified using test cases, data and other models, and subsequently applied to Singapore Strait to simulate a hypothetical oil spill.

Unger, M.A., M.C. Newman, and G.V. Vadas, “Predicting Survival of Grass Shrimp (*Palaemonetes pugio*) Exposed to Naphthalene, Fluorene and Dibenzothiophene”, *Environmental Toxicology and Chemistry*, Vol. 27, No. 8, pp. 1802–1808, 2008.

The composition and persistence of dissolved polycyclic aromatic hydrocarbons released to the water column during oil spills are altered by weathering, tidal transport, and addition of dispersants. Conventional toxicity effect metrics, such as the median lethal concentration ( $\text{LC}_{50}$ ), are inaccurate predictors of mortality from all toxicant exposure duration/concentration combinations likely to occur during spills. In contrast, survival models can predict the proportions of animals dying as a consequence of exposures differing in duration and intensity. Extending previous work with ethylnaphthalene, dimethylnaphthalene, and phenanthrene, survival time models were developed that include exposure duration and concentration to predict time to death for grass shrimp (*Palaemonetes pugio*). Two additional PAHs (naphthalene and fluorene) and a heterocyclic aromatic hydrocarbon (dibenzothiophene) were evaluated. Use of these models confirmed that quantitative structure–activity regression models were possible for predicting

survival model parameters from compound characteristics. Conventional 48-h LC<sub>50</sub>s also were calculated for the compounds and combined with published LC<sub>50</sub>s to predict relative PAH toxicity to *P. pugio* based on octanol–water partitioning.

Venosa, A.D., D.W. King and G.A. Sorial, “The Baffled Flask Test For Dispersant Effectiveness: A Round Robin Evaluation of Reproducibility and Repeatability”, *Spill Science and Technology Bulletin*, Vol. 7, pp. 299-308, 2002.

A round robin testing study of the repeatability of the baffled flask test is described.

Venosa, A.D. and E.L. Holder, “Biodegradability of Dispersed Crude Oil at Two Different Temperatures, *Marine Pollution Bulletin*, Vol. 54, pp. 545-553, 2007.

Laboratory experiments were used to study the biodegradability of oil after dispersants were applied. Two experiments were conducted, one at 20°C and the other at 5°C. In both experiments, only the dispersed oil fraction was investigated. Each experiment included treatment flasks containing 3.5% artificial seawater and crude oil previously dispersed by either Corexit 9500 or JD2000 at a dispersant-to-oil ratio of 1:25. Two different concentrations of dispersed oil were prepared, the dispersed oil then transferred to shake flasks, which were inoculated with a bacterial culture and shaken on a rotary shaker at 200 rpm for several weeks. Periodically, triplicate flasks were removed and sacrificed to determine the residual oil concentration remaining at that time. Oil compositional analysis was performed by gas chromatography/mass spectrometry to quantify the biodegradability. Dispersed oil biodegraded rapidly at 20°C and less rapidly at 5°C. After time, the rate of biodegradation of the undispersed oil was about the same as dispersed oil.

White, D.M., I. Ask and C. Behr-Andres, “Laboratory Study on Dispersant Effectiveness in Alaskan Seawater”, *Journal of Cold Regions Engineering*, Vol. 16, pp. 17-27, 2002.

Dispersant effectiveness was tested at colder water temperatures, 8°C. Corexit 9500, and Alaska North Slope crude oil were tested at 1:10, 1:20 and 1:50. The swirling flask test was used. It was found that dispersant effectiveness was directly proportional to the treatment ratio. The effectiveness was found to drop off when weathering time was increased and a longer contact time was given.

Yakata, N.; Y. Sudo, and H. Tadokoro, “Influence of Dispersants on Bioconcentration Factors of Seven Organic Compounds with Different Lipophilicities and Structures,” *Chemosphere*, Vol. 64, pp. 1885-1891, 2006.

Seven chlorinated compounds with different lipophilicities and structures—1,3,5-trichlorobenzene, pentachlorobenzene, acenaphthylene, 1,4-dimethyl-2-(1-methylphenyl)benzene, 4-ethylbiphenyl, 4,4'-dibromobiphenyl, and 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane were subjected to bioconcentration tests in carp at concentrations below the water solubilities of the compounds in the presence or absence of a dispersant (either an organic solvent or a surfactant). The bioconcentration factors (BCFs) of the compounds were on the order of 10<sup>2</sup>–10<sup>4</sup>. The BCF values remained in the range of 15–49% for all the compounds, whether or not a dispersant was present, i.e., the BCF values in the presence of an organic solvent or a surfactant at a concentration below the critical micelle concentration were not significantly smaller than the BCF values in the absence of the solvent or surfactant.

Yamada, M., H. Takada, K. Toyoda, A. Yoshida, A. Shibata, H. Nomura, M. Wada, M. Nishimura, K. Okamoto and K. Ohwada, “Study on the Fate of Petroleum-Derived Polycyclic Aromatic Hydrocarbons (PAHs) and the Effect of Chemical Dispersant Using an Enclosed Ecosystem, Mesocosm”, *Marine Pollution Bulletin*, Vol. 47, pp. 105-113, 2003.



The fate of PAHs with and without dispersants was investigated in 500 L tanks with seawater. Samples of water and particles were analyzed for 38 PAHs. Low molecular weight PAHs (with less than 3 rings) disappeared rapidly, generally within 2 days. High molecular weight PAHs (with more than 4 rings) remained in the water column for longer times, up to 9 days. Significant portions (10 to 94%) of the high molecular weight PAHs settled to the bottom and were caught in the sediment trap. The addition of chemical dispersant accelerated dissolution of PAHs but amplified the amount of PAHs found in the water column. The water column enrichment factor caused by dispersants was up to 6 times. The increased PAHs appeared to overwhelm the biodegradation and thus higher concentrations were observed in the dispersant-treated tanks throughout the experiment. The dispersant appeared to reduce the amount of heavy PAHs sedimented and put these into the water column.

Yoshida, A., H. Nomura, K. Toyoda, T. Nishino, Y. Seo, M. Yamada, M. Nishimura, M. Wada, K. Okamoto, A. Shibata, H. Takada, K. Kogure and K. Ohwada, "Microbial Responses Using Denaturing Gradient Gel Electrophoresis to Oil and Chemical Dispersant in Enclosed Ecosystems", *Marine Pollution Bulletin*, Vol. 52, pp. 89-95, 2006.

Microbial responses to the addition of oil with or without a chemical dispersant were examined in mesocosm and microcosm experiments by using denaturing gradient gel electrophoresis of bacterial ribosomal DNA and direct cell counting. When a water-soluble fraction of oil was added to seawater, increases in cell density were observed in the first 24 h, followed by a decrease in abundance and a change in bacterial species composition. After addition of an oil-dispersant mixture, increases in cell density and changes in community structure coincided, and the amount of bacteria remained high. These phenomena also occurred in response to addition of only dispersant. These results suggest that the chemical dispersant may be used as a nutrient source by some bacterial groups and may directly or indirectly prevent the growth of other bacterial groups. Thus overall, the effect of dispersant may be to slow biodegradation depending on the type of bacteria present.

## 6.2 Reviewed Conference Proceedings

Abbasova, A., K., Bagirova, G. Campbell, J. Clark, R. Gallagher, N. Garajayeva, A. George-Ares, L. Huseynova, D. Neilson, B. Roddie and R. Tait, "Evaluation of Dispersants for Use in the Azerbaijan Region of the Caspian Sea", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 247-252, 2005.

Dispersant use for the Caspian Sea area was evaluated using the maximum salinity of the area, 12 o/oo. Effectiveness with Chirag crude ranged from 72 to 86% using EPA's baffled flask test. Six dispersants were evaluated, Finasol OSR51, Superdispersant 25, Corexit EC 9527A, Corexit EC 9500A, Slickgone NS and Inipol IP90. Dispersant toxicities for the diatom 72 EC<sub>50</sub> were 18 to 100 mg/L, for a copepod, 48 hr LC<sub>50</sub> were 18 to 208 mg/L and for an amphipod, 48 hr LC<sub>50</sub> were 50 to 100 mg/L. Crude oil and dispersant toxicities were: for the diatom 72 EC<sub>50</sub> were 18 to 100 mg/L, for a copepod, 48 hr LC<sub>50</sub> were 2.1 to 37 mg/L and for an amphipod, 48 hr LC<sub>50</sub> were 20 to 89 mg/L. It was concluded that net environmental benefits would be evaluated for dispersant use in the area.

Addassi, E.N., M. Sowby, H. Parker-Hall, and B. Robberson, "Establishment of Dispersant Use Zones in the State of California- A Consensus Approach for Marine Waters 3 - 200 Nautical Miles from Shore", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 5 p., 2005.

Net Environmental Benefit Analysis (NEBA) is performed for various state zones off the California coast. A comprehensive dispersant use zone was developed for the areas incorporating use zones and zones where there are restrictions on use.

Addassi, E.N., and E. Faurot-Daniels, "California Oil Spill Dispersant Plan - Achievement Through Cooperation", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 5 p., 2005.

Net Environmental Benefit Analysis (NEBA) are performed for various federal zones off the California coast (3 to 200 miles). A comprehensive dispersant use zone was developed for the areas incorporating use zones and zones where there are restrictions on use.

Baca, B., G.A. Ward, C.H. Lane and P.A. Schuler, "Net Environmental Benefit Analysis (NEBA) of Dispersed Oil on Nearshore Tropical Ecosystems Derived From the 20 Year 'Tropic' Field Study", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 453-456, 2005.

The experiment, TROPICS - Tropical Oil Pollution Investigations in Coastal Systems, was reviewed. The experiment involved the deposition of non-treated Prudhoe Bay crude oil and dispersant oil into two separate sites, dominated by nearshore mangrove, seagrass and coral systems in the year 1984. The site was monitored and analyzed after 30 days, 3 months, 2, 6, 10, 17, 18 and 20 years. Oil caused mortality in the short term to invertebrate fauna, seagrass beds, and corals at both the oil and un-oiled sites. This was compared to an un-oiled site. At the untreated site there was some mortality to the mangroves in the first period of time. After 20 years there is still oil at this site and diminished mangrove repopulation. At the dispersed oil site there were no noted effects or oil after 20 years. It was concluded that the use of dispersant in these environments produced a net environmental benefit.

Beasley, K., C. C. Martin, R. Laferriere, "Maximizing Dispersant Preparedness- Lessons Learned from the 2007 Hawaiian Islands Full Scale Exercise", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 805-809, 2008.

This is a review of an exercise conducted in Hawaii to test all aspects of dispersant

preparedness. The exercise included several aspects from the decision making processes, laboratory pre-testing, on-scene test application, application, monitoring, real-time data transmission and post-evaluation.

Belore, R., "Large Wave Tank Dispersant Effectiveness Testing in Cold Water", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 381-385, 2003.

Cold water tests were conducted at OHMSETT using Corexit 9500, Corexit 9527 and fresh and weathered Hibernia and Alaska North Slope crude oils. Twelve tests were completed with effectiveness estimated by the amount of oil left behind in a boom. The author claims that the dispersant application was successful.

Belore, R.C., B.K. Trudel and K. Lee, "Correlating Wave Tank Dispersant Effectiveness Tests with At-Sea Trials", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 65-70, 2005.

At-sea tests in the UK using IFO 180, IFO 380 and the dispersants Corexit 9500, Superdispersant 25 and Agma DR379 were correlated with small tank tests in the authors' facility. One of the purpose of the tests was to examine limiting viscosity, the IFO viscosity was 2000 cP and that of the IFO 380 was 7000 cP. Similar results were achieved, however for there were variances, with the tank test results generally being higher. The tank test results for the IFO 380 were less than 50%, depending on the dispersant dosage. It was noted that the effectiveness of the field tests were estimated using only a 4-point scale and thus correlation is difficult.

Belore, R., A. Lewis, A. Guarino and J. Mullin, "Dispersant Effectiveness Testing on Viscous, U.S. Outer Continental Shelf Crude Oils and Water-In-Oil Emulsions at Ohmsett", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp.823-828, 2008.

Dispersant effectiveness testing on U.S. outer continental shelf oils was carried out both in a small tank and at OHMSETT to study the dispersibility of viscous crude oils. It was concluded that oils with viscosities lower than 6,500 cP were dispersible to a sufficient degree and that oils with viscosity greater than 33,000 Cp were not dispersible. Oils between these two were not available for testing. In OHMSETT, oils with viscosities greater than 10,000 cP were not dispersible. Testing on emulsions showed effectiveness ranged between 10 and 40% with Corexit 9527 being slightly more effectiveness than Corexit 9500.

Belore, R., "Wave Tank Tests to Determine the Effectiveness of Corexit 9500 Dispersant on Hibernia Crude Oil Under Cold Water Conditions", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 735-740, 2002.

Small tank-testing of Hibernia crude oil and using the dispersant Corexit 9500 was carried out in the author's facilities. The temperature was 0 to 1°C and the dispersant to oil ratios were varied. Fresh crude oil dispersed from 96 to 98%, 9.2% evaporated (by volume) dispersed from 89 to 95%, 12.3% evaporated from 25 to 38% evaporated and 27.6% evaporated from 0 to 6%. The cutoff for weathering was estimated to be 10%.

Benns, G., "The Challenges of Implementing Dispersant Effectiveness Monitoring for a Global Response", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 423-426, 2008.

A review of dispersant effectiveness monitoring using fluorometers, as applied to Oil Spill Response and East Asia Response Ltd., is presented.

Bergmann, P. and P. Ross, "Developing Guidelines for Joint Trans-Boundary Resource Agency Input to Dispersant Use, In-Situ Burning, and Places of Refuge Decision-Making- The Canada-United States Dixon Entrance Example", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp.597-601, 2008.

Joint Canada-U.S. guidelines for the use of in-situ burning, dispersants and places of refuge have been developed for the Dixon entrance area.

Boufadel, M.C., E. Wickley-Olsen, T. King, Z. Li, K. Lee, A.D. Venosa, "Theoretical Foundation for Predicting Dispersion Effectiveness due to Waves", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 509-513, 2008.

A model of oil dispersion or droplet formation in wave tanks is presented. It is noted that there is not a theoretical basis for such a model, because oil breakup studies were based on small constant-energy systems. Under a wave regime, energy varies. A droplet model is developed that uses a varying energy input such as from a wave. The model is illustrated using simulated wave data. It is concluded that the model requires testing and calibration in real systems.

Brekne, T. M., S. Holmemo, and G.M. Skeie, "Optimizing Offshore Combat of Oil Spills and Development of New Booms and Helicopter Based Application of Dispersants", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 6 p., 2003.

New developments in Norwegian offshore countermeasures are reviewed. As part of this development a system of helicopter-based dispersant application systems will be placed offshore. The entire system will be supplied and operated from offshore platforms.

Chandrasekar, S., G. Sorial and J.W. Weaver, "Determining Dispersant Effectiveness Data for a Suite of Environmental Conditions", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 331-334, 2003.

A baffled flask test was used to conduct a series of studies on various factors influencing dispersion. The factors of temperature, oil type, oil weathering, dispersant type and rotation speed were related to the dispersant effectiveness. Three oils were used: Diesel, South Louisiana crude and Prudhoe Bay crude as well as two different dispersants, unidentified. Data analysis shows that for most oils, temperature, mixing energy and weathering were important factors. Empirical relationships between dispersion amount and the variables were developed.

Clark, J., K. Becker and D. Lessard, "Maintaining Dispersant Stockpiles and Assessing their Quality", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 695-698, 2008.

Dispersants in storage may deteriorate due to high temperatures or other unfavorable conditions. Several recommendations are given to ensure that the quality of the dispersant has not or will not degrade in the future. 1. Develop a storage system that minimizes the possibility that the dispersant is subjected to high or low temperatures, and high humidities. 2. Check the integrity of storage containers on a regular basis. 3. Rotate stock periodically. And 4. Analyze the stock regularly for effectiveness.

Clark, J. and A. Venosa, "Assessing Dispersant Effectiveness for Heavy Fuel Oils Using Small-Scale Laboratory Tests", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 59-63, 2005.

Laboratory effectiveness testing of three dispersants, Corexit 9500, Superdispersant 25 and Agma Dr 379, were carried out using the swirling flask test, the baffled flask test, the Warren

Springs test and the EXDET test. The oils used were IFO 180 and 380. Although the paper states that rank of dispersant effectiveness is not preserved in all tests, examination of the data shows that the best dispersants were the same in all 4 tests. The ability to disperse IFO 380 varied with the amount of energy available in the tests. The higher energy tests could disperse some of the IFO 380.

Clark, J., B. Dahl and W.M. Lerch, "Tier 1 Response Equipment Strategies for Smaller, Fuels and Lubes Marine Terminals", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 6 p., 2003.

Tier I (USA small spills) spill response is reviewed. Strategies and selection of response equipment for on-water response are given. It is emphasized that Tier I response should employ light, portable and simple equipment. Recommendations are given for gasolines, middle distillate fuels and heavy fuel. Dispersants might be used on the latter two fuels given correct conditions and 2 barrels of dispersant might be stocked.

Colcomb, K., M. Peddar, D. Salt and A. Lewis, "Determination of the Limiting Oil Viscosity for Chemical Dispersion at Sea", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 53-58, 2005.

Small-scale tests were carried out offshore to evaluate the dispersibility of IFO 180 and IFO 380. Slicks were treated with different ratios of one of three dispersants. The effectiveness was rated visually by a panel of judges on a boat closely following the application.

Analysis of this data by the present author shows that only the data from dispersant C correlates to a degree and also with the viscosity of the oil. The data for dispersant A correlates poorly and that for dispersant B correlates inversely, that is effectiveness increases with viscosity, but the correlation is poor.

Colcomb, K., "Very Heavy Fuel Oil- UK Spill Risk Assessment", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 717-723, 2008.

An assessment of the very heavy fuel oils now being transported around the UK was presented. The production, transport and use of these fuels are increasing. It was noted that dispersants were not effective on these oils and therefore, other countermeasures were needed.

Colcomb, K., "The NAPOLI Incident, Devon UK 2007 - The Formal NCP Environment Group", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 103-107, 2008.

The development of an environmental group to deal with scientific issues at spill scenes was first demonstrated at the Napoli incident. This group relates to dispersants in that they are involved in decisions to use dispersants and include testing, monitoring and looking at physical effects of such action.

Cooper, D., V. Volchek, S. Cathum, H. Peng and J. Lane, "Trace Dispersant Detection and Removal", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 799-812, 2003.

Testing was carried out to see if membrane technology could be used to remove surfactants from water after dispersant experiments. It was found that the G50 membrane had poorest dispersant and oil rejection although it had highest permeate flux. The NF45, Desal 5, G10, and G20 had very good rejection, with the G20 having the highest flux rate of the four. Because of these facts, the G20 was selected as the recommended membrane for the OHMSETT application.

The results of the membrane testing indicate that it is possible to separate surfactants from water using membrane technology. Problems with relatively low flux rates, however, indicate that a relatively large membrane system would be required to clean the OHMSETT tank. A preliminary cost estimate was obtained for a system with the following parameters: Membrane: G20 (Osmonics, Inc.; MWCO: 3500 Daltons), permeate flux of 20L/m<sup>2</sup>/hr, with a volume recovery of 90%. Pilot scale testing would be recommended to provide cost estimates due to scaling factors.

Dale, D., and A. Allen, "Dispersant Mission Planner, DMP2", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 791-796, 2008.

The dispersant mission planner - version 2 - is a computer aid is used for the assessment of the logistics of a dispersant operation. It can be used to calculate the number of application vehicles, aircraft or ships, needed for an operation and 'effective daily application capacity'. The latter is the capacity of a single application platform to deal with oil slicks. The model yields output in accordance with U.S. Coast Guard requirements.

Daling, P.S., I. Singaas, M. Reed and O. Hansen, "Experiences in Dispersant Treatment of Experimental Oil Spills", *Spill Science and Technology Bulletin*, Vol. 7, pp. 201-213, 2002.

This paper is a review of prior work in Norway to examine dispersants. Field trials conducted in 1994, 1995, and 1996 are reviewed. The lessons from these field trials are given.

DeHaven, L., and R. Tirrell, "How to List a New Product on the National Oil and Hazardous Pollution, Subpart J Product Schedule", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 657-660, 2008.

In the USA, treatment products must be listed on the product schedule. This paper outlines the requirements to list products and the testing that must be done.

Dewhirst, S., "Design Implementation and Use of a Practical Tier Two Aerial Dispersant and Surveillance Service in West and Central Africa", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2005.

The practical issues of applying dispersant in another country are summarized. These issues include, trans-boundary shipment of goods and materials, logistics and location of depots and cooperation needed. The solutions include: pre-spill training, development of cooperation among agencies and development of a good plan.

Ebert, T.A., R. Downer, J. Clark and C.A. Huber, "Summary of Studies of Corexit Dispersant Droplet Impact Behavior into Oil Slicks and Dispersant Droplet Evaporation", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 797-800, 2008.

This is a summary of two studies. The first was to characterize the breakthrough of dispersant droplets of various sizes. through oil films of various thicknesses. The oil used was IFO 380. It was found that droplets with diameters of 1,000 micrometers would not pass through an oil slick of 0.01 mm, and that a slick thickness of 0.2 mm will prevent up to 2,000 micrometer droplets from passing through this heavy oil. The second study compared the evaporation rates of Corexit 9500 and 9527 with water evaporation over a 20-minute period. At about 35°C, droplets of dispersant from 0.25 to 1 µL showed 2 to 10% loss for Corexit 9500 and 28 to 35% loss for Corexit 9527. At lower temperatures no evaporative loss was noted.

Etkin, D. S., D. French McCay, N. Whittier, S. Sankaranarayanan, and J. Jennings, "Modeling of Response, Socioeconomic, and Natural Resource Damage Costs for Hypothetical Oil Spill Scenarios in San Francisco Bay", in

*Proceedings of the Twenty-fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1075-1102, 2002.

Response and socioeconomic costs were estimated for San Francisco Bay for 3 spill sizes and four oil types. The spread of oil and shoreline oil were modeled using SIMAP. It was found that response costs were higher for mechanical operations compared to dispersants for the heavier oils. For the diesel and gasoline spills the response costs comprised about 20% of the total compared to about double that for the crude and heavy fuel oil. Socioeconomic costs were about 60 to 75% of costs for the lighter products and 45 to about 55% for the heavier oils.

Fieldhouse, B., "Dispersion Characteristics of Oil Treated with Surface Washing Agents for Shoreline Cleanup", in *Proceedings of the Thirty-first Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 373-394, 2008.

A protocol was developed to produce oil-in-water dispersions from treatment of a heavy oil with a surface washing agent. The entire volume of oil is removed from the test substrate during treatment and transferred to the water column. The test is used to evaluate the dispersion characteristics of Corexit 9580. Dispersion stability was assessed by quantifying the change in oil concentration over time as the oil rises to the water surface. Within the context of shoreline treatment, it is shown that Corexit 9580 forms somewhat stable oil-in-water emulsions during treatment of heavy oils. The dispersions produced, rise in quiescent conditions over periods numbered in hours. In addition, the resurfaced oil does not entirely separate, but remains as stable droplets that are easily re-dispersed. The test parameters varied were the surface washing agent product dosage, test temperature, water salinity and test oil type. Each appears to influence the rate of oil droplet resurfacing, but not to an operationally significant degree. Two alternative surface washing products were tested for comparison, one containing surfactants, the other without. The dispersion produced by the surfactant-containing product PES-51 mostly resolved to oil and water in minutes, whereas the CytoSol product was far less effective, and tended to have dispersion characteristics closer to those of C9580.

Fingas, M.F., B. Fieldhouse, L. Sigouin, Z. Wang and J.V. Mullin, "Dispersant Effectiveness Testing: Laboratory Studies of Fresh and Weathered Oils", in *Proceedings of the Twenty-Fourth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 551-566, 2001.

Recent results of dispersant testing are reviewed, including testing of several new oils for effectiveness and the test of several weathered oils for effectiveness. The swirling flask test has been used to measure the effectiveness of these oils in the laboratory. The dispersant used was Corexit 9500. The results show the typical trends of decrease in effectiveness with weathering. The weathering trend is shown to be characteristic of that oil and cannot be predicted by correlation with simple physical properties of the starting oil.

Fingas, M., B. Fieldhouse and Z. Wang, "Dispersant Testing: Study on Analytical and Test Procedures", in *Proceedings of the Twenty-Seventh Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 807-817, 2004.

The analytical procedure for the Swirling Flask Test was reviewed. A re-examination of the analytical procedure shows that the integration method could be improved by integrating the entire chromatogram rather than just peaks. The result of the method improvement is to decrease the maximum variation of about 5% down to about 2%. A second feature of the swirling flask test, the side spout was studied by testing with a new vessel with no side spout but with a septum port. The effect of this was to decrease the variability somewhat, but also to decrease the energy

and mixing in the vessel. It is suggested that the spoutless vessel might be considered as a separate test, rather than a variation of the swirling flask.

Fingas, M. and L. Ka'aihue, "Dispersant Tank Testing: A Review of Procedures and Consideration", in *Proceedings of the Twenty-Seventh Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1003-1016, 2004.

This paper is a perspective on testing the effectiveness of oil spill dispersants in large tanks. Literature that relates to testing methodology is reviewed. The following 17 critical factors need to be considered and included in any test for measuring the effectiveness of dispersants in a tank in order for that test to be valid. These factors are reviewed in this assessment:

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

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

Fingas, M.F., and L. Ka'aihue, "Weather Windows for Oil Spill Countermeasures", in *Proceedings of the Twenty-Seventh Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 881-955, 2004.

Oil spill countermeasures are affected by weather such that, in some cases, these countermeasures cannot continue under adverse weather conditions. A literature review was carried out to determine if there were data related to the performance of all countermeasure techniques under varying weather conditions. More than 1000 pieces of literature were surveyed and, of these, more than 230 papers contained useful information. Although the literature did not provide any quantitative guides for the performance of countermeasures under varying weather conditions, data could be extracted to enable assessment of changes in their performance related to weather conditions. The most important factors influencing countermeasures are wind and wave height. These two factors are related and, given sufficient time for the sea to become 'fully-arisen', can be inter-converted. These factors must sometimes be considered separately, however, so that specific weather effects can be examined. Other weather conditions affecting



countermeasures include currents and temperature. Currents are important as they become the critical factor for certain countermeasures such as booms. Temperature primarily affects the performance of dispersants and has been shown to have only minimal effect on other countermeasures. The weather affects dispersant application and effectiveness in three ways: the amount of dispersant that contacts the target is highly wind-dependent; the amount of oil dispersed is very dependent on ocean turbulence and other energy; and the amount of oil remaining in the water column is dependent on the same energy. Nomograms for dispersant effectiveness have been created. At high sea energies, natural dispersion is very much a factor for lighter oils. The effects of weather on other countermeasure methods have been summarized.

Fingas, M., B. Fieldhouse and Z. Wang, "The Effectiveness of Oil Spill Dispersants on Alaskan North Slope Crude Oils Under Various Temperature and Salinity Regimes", in *Proceedings of the Twenty-Ninth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, pp.821-826, 2006.

The effectiveness of dispersion for Alaska North Slope oil at different temperatures and salinity has been measured. The finding of this study is that there is an interaction between salinity and effectiveness for Alaska North Slope crude oil. The variation of temperature and salinity were correlated and a prediction scheme developed.

Fingas, M., B. Fieldhouse and Z. Wang, "The Effectiveness of Oil Spill Dispersants Under Various Temperature and Salinity Regimes", in *Proceedings of the Twenty-Eighth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, pp. 377-391, 2005.

The effectiveness of dispersion of Corexit 9500 on ASMB at different temperatures and salinity has been measured using the ASTM standard test. The results of this are compared to the only one historical test reported in the literature, in which both the temperature and salinity were varied over a broad range of values. This historical test concluded that there may be an interaction between temperature and salinity such that the traditional smooth curves for salinity and temperature behaviour were not preserved. The finding of this series of tests is that there is interaction between salinity, temperature and effectiveness. The variation of temperature and salinity is best taken together for accurate prediction.

Fingas, M. and L. Ka'aihue, "Review of Monitoring Protocols for Dispersant Effectiveness", in *Proceedings of the Twenty-Seventh Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, pp. 977-1002, 2004.

This 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 SMART monitoring protocol from a number of USA government agencies. The protocols currently consist of some visual criteria and often include a sub-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. 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.

Fingas, M. and L. Ka'aihue, "Dispersant Field Testing: A Review of Procedures and Consideration", in *Proceedings of the Twenty-Seventh Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1017-1046, 2004.

This white paper provides a perspective on field testing of the effectiveness of oil spill dispersants. All field tests conducted to date are briefly reviewed and literature that relates to testing methodology is cited. The following 25 aspects of the field testing of dispersants are discussed.

- |   |  |
|---|--|
| 1. Mass balance                                 | 14. Visibility of oil from the surface     |
| 2. Proper controls                              | 15. Background levels of hydrocarbons      |
| 3. Analytical method                            | 16. Fluorescence of dispersant             |
| 4. Differential plume movement                  | 17. Herding                                |
| 5. Time lag and length of time followed         | 18. Emulsion breaking                      |
| 6. Mathematics of calculation and integration   | 19. Success of application                 |
| 7. Lower and upper limits of analytical methods | 20. Heterogeneity of slick and plume       |
| 8. Use of remote sensing                        | 21. Deposition measurements                |
| 9. Thickness measurement                        | 22. True analytical standards              |
| 10. Behaviour of oil with surfactant content    | 23. Effect of wind on dispersant and slick |
| 11. Surfactant stripping                        | 24. Dispersant runoff                      |
| 12. Tracking surface oil and dispersed oil      | 25. Weathering of the oil                  |
| 13. Recovering surface oil                      |  |

Each of these factors is important to the appropriate outcome of the dispersant field experiment. The most important factors are the ability to determine a mass balance, use of proper controls and analytical methods, and avoiding procedures that will result in incorrect results. Experimental design is discussed throughout this paper. Two experimental designs are described that are very poor and that would result in very large errors. The first one, the measurement of surface oil remaining after dispersant application on oil contained in a boom, is flawed given that the currents/waves are near the critical loss velocity. Equations are given that show the loss of oil is strongly affected by the surface tension. This test as described is largely measuring containment loss and not dispersant effectiveness. The second experimental design that results in very large errors is the integration of dispersed oil under the slick. The dispersed oil plume and slick do not have the same geometries and also often have different trajectories. Integration under the slick overestimates the dispersion by as much as a factor of 10.

Two tests that could yield useful results are summarized. The first is a steady-state discharge of oil and dispersant in a constant current. The plume can be measured by in-situ fluorometry and integration. Since there is a steady state, this measurement can be taken at several points along the plume to confirm the effectiveness. The second is a test in which the concentration of oil in the water column after about 24 hours is used to define effectiveness. This method can be applied only in confined areas such as a test tank. This paper points out the technology and understanding that is necessary to conduct an accurate dispersant field test. There are many nuances involved in

conducting such a test. These relate to good chemistry and physics and an understanding of the processes involved.

Fingas, M.F., and L. Ka'aihue, "Oil Spill Dispersion Stability and Oil Re-surfacing", in *Proceedings of the Twenty-ninth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 729-819, 2006.

Fingas, M., "Oil Spill Dispersion Stability and Oil Re-surfacing", in *Proceedings of The 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 661-665, 2008.

These papers review the literature on the well-known phenomenon that chemically dispersed oil destabilizes after the initial dispersion. The destabilization of oil-in-water emulsions such as chemical oil dispersions is a consequence of the fact that not all emulsions are thermodynamically stable. Ultimately, natural forces move the emulsions to a stable state, which consists of separated oil and water. The rate at which this occurs is important. An emulsion that stays sufficiently stable until long past its practical use consideration may be said to be kinetically stable. Kinetic stability is a consideration when describing an emulsion. An emulsion is said to be kinetically stable when significant separation (usually considered to be half or 50% of the dispersed phase) occurs outside of the usable time.

There are several forces and processes that result in the destabilization and resurfacing of oil-in-water emulsions such as chemically dispersed oils. These include gravitational forces, surfactant interchange with water and subsequent loss of surfactant to the water column, creaming, coalescence, flocculation, Ostwald ripening, and sedimentation.

Gravitational separation is the most important force in the resurfacing of oil droplets from crude oil-in-water emulsions such as dispersions and is therefore the most important destabilization mechanism. Droplets in an emulsion tend to move upwards when their density is lower than that of water. This is true for all crude oil and petroleum dispersions that have droplets with a density lower than that of the surrounding water. More dense oils, which would sink as emulsions, are poorly, if at all, dispersible. The rate at which oil droplets will rise due to gravitational forces is dependent on the difference in density of the oil droplet and the water, the size of the droplets (Stokes' Law), and the rheology of the continuous phase. The rise rate is also influenced by the hydrodynamical and colloidal interactions between droplets, the physical state of the droplets, the rheology of the dispersed phase, the electrical charge on the droplets, and the nature of the interfacial membrane.

Creaming is the destabilization process that is simply described by the appearance of the starting dispersed phase at the surface, without the processes in the intervening spaces being described. In the oil spill world, creaming is the process that might be described as resurfacing.

Coalescence is another important destabilization process, which has been studied extensively in oil-in-water emulsions. Two droplets that interact as a result of close proximity or collision can form a new larger droplet. The end result is to increase the droplet size and thus the rise rate, resulting in accelerated destabilization of the emulsion. Studies show that coalescence increases with increasing turbidity as collisions between particles become significantly more frequent.

Ostwald ripening is another process in the destabilization of oil-in-water emulsions. Ostwald ripening occurs when the larger droplets in an emulsion grow due to absorption of soluble components or very small droplets from the water column. The effect is to remove soluble material from the water column and smaller droplets, resulting in an increased growth of the larger droplets. The phenomenon occurs because the soluble components of the dispersed phase

are more soluble in the larger droplets than in the water and the smaller droplets. Although the Ostwald ripening phenomenon has not been investigated with oil-in-water emulsions to the same extent as other phenomena, it is believed to be important.

Another important phenomenon when considering the stability of dispersed oil is the absorption/desorption of surfactant from the oil/water interface. This process is stated to be the most important process for chemical considerations of surfactants and interfacial chemistry. When surfactants are dissolved in a bulk phase such as water, they start to be absorbed at the oil surface or interface. The system moves toward equilibrium, that is equilibrium amounts of surfactant at the interface and in the bulk phase. Desorption occurs primarily as a result of the lower concentration of surfactants in the bulk phase or water. The surfactants will transfer back and forth from the oil/water interface until an equilibrium of concentration is established in the interface or in the bulk liquid (water). It is well known that in dilute solutions, much of the surfactant in the dispersed droplets ultimately partitions to the water column and thus is lost to the dispersion process. Little, if any, surfactant would partition back into the droplet in a dilute solution, which is the case for oil dispersions at sea. This is one important difference between dilute and concentrated solutions. This report provides examples of studies and models in all the processes as well as data from experiments and calculations. Data show that for a dilute solution such as a chemically dispersed oil spill, half-lives could vary from 2 to 24 hours, with a typical average value of 12 hours.

Fingas, M., Z. Wang, B. Fieldhouse and P. Smith, "The Correlation of Chemical Characteristics of an Oil to Dispersant Effectiveness", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 679-730, 2003.

The dispersant effectiveness data on 295 oils and their chemical and physical properties were correlated with 29 properties to develop a prediction equation. The dispersibility of Corexit 9500 in the swirling flask apparatus was used as the key parameter. The highest correlation parameters were achieved with the content of nC12, naphthalenes, inversely with C26, the PAHs, and the sum of C12 to C18 hydrocarbons. This is highly indicative that the smaller aliphatic hydrocarbons up to C18 and the PAHs are the most dispersible components of oil. Furthermore, aliphatic hydrocarbons greater than C20 correlate inversely with the dispersant effectiveness, indicating that these hydrocarbons suppress dispersion. Thirteen models were constructed to predict the chemical dispersibility of oils. The simplest and best model is:

Corexit 9500 dispersibility (%) =  $-11.1 - 3.19(\ln \text{C12 content}) + 0.00361(\text{naphthalene content in ppm}) - 7.62(\text{PAH content squared}) + 0.115(\text{C12 to C18 content squared}) + 0.785(\% \text{fraction oil boiling below } 250^{\circ}\text{C})$ .

Models ranged from simple predictors involving only two parameters such as viscosity and density to 14-parameter models. The models developed were analysed statistically and the effectiveness was calculated for several dispersants. The more sophisticated models are able to predict dispersant effectiveness with high accuracy.

Fingas, M., G. Thouin, Z. Wang and B. Fieldhouse, "Dispersed Oil Resurfacing With Time", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 731-742, 2003.

Resurfacing was examined using the swirling flask test. Resurfacing was examined at 14 time intervals up to 96 hours. Two oils were used for the tests, Alberta Sweet Mixed Blend standard and North Slope Crude oil. Dispersants Corexit 9500 and Corexit 9527 were used in this

study. Results show that under all conditions, that significant amounts of oil resurfaces after the initial dispersion takes place. Mixing has a tendency to retain more oil in the water column, however only about 8% more oil is retained in the water column than if the system is static over the 96-hour test period. Mathematical correlations were developed to describe the process and to provide prediction capability. The equation for shaken samples is:

$$\text{Effectiveness at time (\%)} = -4 + 12 \cdot \ln(\text{standard value}) - 5 \cdot \ln(\text{time in hours}) \quad (1)$$

and for the static samples:

$$\text{Effectiveness at time (\%)} = -33 + 13 \cdot \ln(\text{standard value}) + 8/(\text{time in hours}) \quad (2).$$

The standard value is the effectiveness measured at the specified time of 20 minutes in the swirling flask.

Fingas, M., L. Sigouin, Z. Wang and G. Thouin, "Resurfacing of Dispersed Oil With Time in the Swirling Flask", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 773-783, 2002.

Chemically-dispersed oil destabilizes due to the loss of surfactants to the water column. Once droplets lose a critical amount of surfactant they can re-coalesce and are less likely to remain in the water column. This varies with the amount of energy applied, however, a significant amount of oil still resurfaces. Resurfacing was examined using the swirling flask test. Resurfacing was examined at 10 time intervals up to 48 hours. Two oils were used for the tests, Alberta Sweet Mixed Blend standard and North Slope Crude oil. Corexit 9500 and Corexit 9527 were used in this study. Results show that under all conditions, that significant amounts of oil resurfaces after the initial dispersion takes place. Mixing has a tendency to retain more oil in the water column, however only about 10% more oil is retained in the water column than if the system is static. Mathematical correlations were developed to describe the process and to provide prediction capability.

Fingas, M.F., "Energy and Work in Laboratory Vessels", in *Proceedings of the Twenty-Seventh Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1-18, 2004.

Fingas, M.F. "Measurement of Energy in Laboratory Vessels - III", in *Proceedings of the Twenty-eighth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp.1-16, 2005.

Energy and work are calculated or estimated in several laboratory vessels and compared to estimates of energy/work at sea. Some measurements completed by PIV and anemometry are compared to these calculated values. The initial measurements and estimates indicate that the energy in several laboratory vessels is similar and that it may be equivalent to those encountered at sea under moderate wind and wave conditions. Two techniques have been initiated to measure energy. The measurement technique chosen to do this is Particle Image Velocimetry or PIV. In this method, seed particles - which could be oil droplets, are put into the fluid and the fluid is illuminated with a laser. The movement of a particle in a given cell is measured as a function of time. This can occur as fast as 30 to 100 Hz, depending on the apparatus. Turbulent energy can be calculated at each point in the image frame. The other method used is the method of using hot wire anemometry. This method can yield data similar to PIV, however requires the intrusion of a probe into the area. The methods are compared in several laboratory vessels under several energy conditions, results are summarized in the table below:

Table 2 Work, Energy and Turbulence Levels of Various Laboratory Apparatuses													
						Adjusted for Volume /L			Experimental				
Apparatus	Use	Energy	Typical rpm	Water	Calculated	Calculated	Calculated	Calculated	Energy	dual probe	Near surface	Energy	PIV
		Application	Setting	Volume	Work input	Level	Work input	Level	Dissipation	%	Energy	%	Data
			rpm	mL	Joules/min	Joules	Joules/Lmin	Joules/L	U and V sum	Tested	Total	Tested	Tested
Swirling Flask	Dispersant screening	moving table	150	120	0.35	3.50E-05	2.9	2.92E-04	6.50E-04	360	1.40E-04	105	90
Septum Flask	Dispersant screening	moving table	150	120	0.17	3.50E-05	1.4	2.92E-04	5.67E-04	781	1.00E-04	70	
Standard Beaker	Various	moving table	150	400	1.2	1.20E-04	3	3.00E-04				90	80
Emulsion Unit	Emulsion formation	end-over-end rotation	50	600	22.8	0.05	38	8.33E-02					
Labofina Unit	Dispersant screening	end-over-end rotation	50	250	4.56	0.01	18.2	4.00E-02					
High Energy Unit	Dispersant physics	moving table	100-250 150 average	5000	294	8.22E-03	58.8	1.64E-03					
Tank	Large-scale testing	agitator	120	300000	33	0.28	0.11	9.33E-04	8.22E-03	376	5.90E-02	40	
			240	300000	66	1.1	0.22	3.67E-03	1.23E-02	467	2.00E-01	5	
			480	300000	132	4.5	0.44	1.50E-02	1.77E-02	322	6.00E-01	38	
Tank	Large-scale testing	oscillating loop	60 strokes	300000	18	0.9	0.06	3.00E-03					
The following are approximations based on estimation equations given in the paper													
Wind equivalent	comparison	over water	5 m/s	1000	1.2	0.0001	1.2	1.00E-04					
			10 m/s	1000	4.9	0.0002	4.9	2.00E-04					
			20 m/s	1000	20	0.0004	20	4.00E-04					
			30 m/s	1000	44	0.0016	44	1.60E-03					
			40 m/s	1000	78	0.0064	78	6.40E-03					
Wave Height Equivalent	comparison	per meter wave height	0.5	1000	1.2	0.0001	1.2	1.00E-04					
			1	1000	4.9	0.0002	4.9	2.00E-04					
			2	1000	20	0.0004	20	4.00E-04					
			3	1000	44	0.0016	44	1.60E-03					
			4	1000	78	0.0064	78	6.40E-03					

Fingas, M. and L. Ka'aihue, "A Literature Review of the Variation of Dispersant Effectiveness With Salinity", in *Proceedings of the Twenty-Eighth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, pp. 657-678, 2005.

This paper is a literature review of the effects of water salinity on chemical dispersion, especially those effects related to effectiveness. Literature shows that testing of effectiveness with salinity variation consistently shows a decrease in effectiveness at lower salinities and a decrease after a maximum salinity is reached between about 20 to 40 o/oo. The general surfactant literature was also reviewed for the effects of salinity on surfactants and surfactant phenomena. There is a body of literature on the use of surfactants for secondary oil recovery. There are some commonalities among the many findings. Recovery efficiency falls off at both high and low salinities. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant. Several studies on the interaction of specific hydrocarbons and surfactants were reviewed. The consensus of these papers is that the solubility of the hydrocarbon increases with increasing salinity and is low at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25 to 35 o/oo. A number of physical systems involving surfactants and salinity changes are reported in the literature. Included in these is the finding that the stability of microemulsions is greater at salinities of 25 to 35 o/oo. Some workers found that the stability of systems was very low in fresh water or in water with salinities of < 10 o/oo. This is consistent with the findings in the oil spill literature.

Fingas, M.F., "Energy and Work Input into Laboratory Vessels" in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 663-669, 2005.

Turbulent and total energy are known to be a very important part of the measurement of oil spill

processes. Two techniques have been initiated to measure energy. The measurement technique chosen to do this is Particle Image Velocimetry or PIV. In this method, seed particles are put into the fluid and the fluid is illuminated with a laser. The movement of a particle in a given cell is measured as a function of time. Energy can be calculated from at least 2 successive frames. Turbulent energy can be calculated at each point in the image frame (from about 100 to 500 points). The other method used is the method of using hot wire anemometry. This method can yield data similar to PIV, however requires the intrusion of a probe into the area. The measurements are compared to calculations based on formulations presented in the literature. An important point is that it is shown that a single value does not represent the energy in a vessel (or at sea) because the energy level is not homogeneous throughout the field nor is it simply described. Several of the laboratory vessels have energy fields that are representative of sea conditions.

Fingas, M.F., "Estimation of Oil Spill Behaviour Parameters from Readily-available Oil Properties", in *Proceedings of the Thirtieth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1-34, 2007.

Often oil behaviour parameters such as for evaporation, emulsification and chemical dispersion, are needed and specific behavioural data are not available. Often only basic data such as density, and viscosity are available. This paper presents a series of simple schemes to provide prediction for oil evaporation, emulsification and chemical dispersion given readily-available data. Schemes for prediction are given using only density and viscosity and then adding SARA and other composition data. As the input data amount is increased, more accuracy in the estimations are achieved. The estimation schemes are compared to the measured data available and also to the use of generic oil types sometimes used in models such as 'light or heavy crude oil'. It was found that the accuracy of these estimation schemes are more accurate than the traditional predictions based on generic oil types.

French McCay, D., W. Nordhausen, J.R. Payne and J.J. Rowe, "Modeling Potential Impacts of Effective Dispersant Use on Aquatic Biota", in *Proceedings of the Twenty-Ninth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, pp. 855-878, 2006.

Model estimates of the concentrations of hydrocarbons that would be expected in the surface mixed layer for large volumes of dispersed oil. This was taken as one large load of dispersant from an aircraft on light Arabian crude oil. Various effectiveness options were chosen and various weather and sea conditions. Impacts on water-column species was predicted for the various options. For all conditions and no dispersant application, it was predicted that there would be little biological impact. The highest water column impacts would occur with chemical dispersant application and light winds. This condition would result in the least and slowest dilution. The impacted water column was predicted to be 70 to 200 million m<sup>3</sup> water.

French-McCay, D.P. and J.R. Payne, "Model of Oil Fate and Water Concentrations With and Without Application of Dispersants", in *Proceedings of the Twenty-Fourth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 611-645, 2001.

A three-dimensional model is used to predict oil behaviour and water column oil concentrations from oil spills when dispersants are applied or not applied. The focus is on weathering algorithms and how the dispersant application changes the outcome of the physical properties and ultimate fate of oil spills with or without dispersant use.

French-McCay, D., J.J. Rowe, N. Whittier, S. Sankaranarayanan, D.S. Etkin and L. Pilkey-Jarvis, "Evaluation of the Consequences of Various Response Options Using Modeling of Fate, Effects, and NRDA Costs of Oil Spills into Washington Waters", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 5 p., 2005.

A three-dimensional model was used to predict oil behaviour and water column oil concentrations from oil spills when dispersants are applied or not applied on hypothetical spills in Washington State waters. The focus was on aspects such as costs, socioeconomic costs. This information is generated to assist in decision-making on the use of dispersants.

French-McCay, D., C. Mueller, J. Payne, E. Terrill, M. Otero, S.Y. Kim, W. Nordhausen, M. Lampinen, and C. Ohlman, "Dispersed Oil Transport Modeling Calibrated by Field-Collected Data Measuring Fluorescein Dye Dispersion", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 527-536, 2008.

Fluorescent dye dispersion data gathered off San Diego was combined with surface currents from high-frequency radar to calibrate oil transport models. It was noted that the dye plume quickly extended throughout an upper mixed layer (about 7 to 15 m). The horizontal movement was measured by looking at HF measurements of drogues set to the outside of the horizontal extent of the plume. This data was used to calibrate oil transport models, but it was noted that other factors such as current shears would have to be accounted for. Further, this paper would benefit from discussion of how dye diffusion relates to oil droplet diffusion as there is orders-of-magnitude difference in particle size.

French-McCay, D.P. "Modeling Evaluation of Water Concentrations and Impacts Resulting From Oil Spills With and Without the Application of Dispersants", in *Proceedings of the Fifth International Marine Environmental Modelling Seminar*, SINTEF Applied Chemistry, Trondheim, Norway, pp. 53-84, 2001.

A three-dimensional model (SIMAP) is used to predict oil behaviour and water column oil concentrations from oil spills when dispersants are applied or not applied. The focus is on weathering algorithms and how the dispersant application changes the outcome of the physical properties and ultimate fate of oil spills with or without dispersant use.

French-McCay, D., N. Whittier, C. Dalton, J. Rowe, S. Sankaranarayanan and D. Aurand, "Modelling Fates and Impacts of Hypothetical Oil Spills in Delaware, Florida, Texas, California and Alaska Waters, Varying Response Options Including Use of Dispersants", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 735-740, 2005.

The modeling of oil spill response, including the effects of dispersant application is carried out in 5 areas of the USA, this paper focused on Florida. Both oil spill plume and atmospheric modeling are carried out to assess the impacts including the concern to biological species, habitats, human health and socioeconomic resources. Variables included spill volume, weather, response options and current inputs.

Fuller, C.B., J.S. Bonner, J.D. Bujnoch, S.F. Ussery, G. Arrambide and M.C. Sterling, "A Re-Circulated Toxicity Exposure Chamber to Evaluate Hydrocarbon Dispersions", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 865-875, 2002.

A new chamber was designed to evaluate the toxicity of dispersed oil. As a test, *Menidia beryllina*, were exposed to oil and no oil regimes. The no oil exposure resulted in only 2% mortality after 96 hours, whereas the exposure to chemically-dispersed oil result in 97% mortality after 96 hours.

Fuller, C., J. Bonner, F. Kelly, C. Page, and T. Ojo, "Real Time Geo-Referenced Detection of Dispersed Oil Plumes",



in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2005.

A system of GPS-annotated and recorded fluorometry was developed and demonstrated. A comparison of two in-situ fluorometers was carried out in a test tank and demonstrated during an exercise.

George-Ares, A., E.J. Febbo, D.J. Letinski, J. Yarusinsky, R.S. Safadi, and A.F. Aita, "Use of Brine Shrimp (*Artemia*) in Dispersant Toxicity Tests- Some Caveats", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2003.

Caution is advised in designing toxicity tests using brine shrimp, *Artemia*, as test conditions can change the results. The type of seawater used can affect results. When natural seawater is used the LC<sub>50</sub> values ranged from 35 to 147 ppm, but were from 29 to 39 when artificial seawater was used. The age of the nauplii is another test variable that can be affected. The 48-hour old nauplii is more sensitive than the 24 hour nauplii. This also varies with salinity and temperature conditions.

Goodman, R. H., "Is SMART Really that Smart?", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 779-786, 2003.

The SMART monitoring protocol is reviewed. It is concluded that, even under the best conditions, the collected data would provide little or no useful information for the decision make, either in terms of response effectiveness or net environmental benefit. It is also concluded that such monitoring protocols retard the spill response operation.

Goodman, R., "Mass Balance and Dispersant Effectiveness: Are New Techniques and Methodologies Needed?", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 177-181, 2005.

Mass balance in measuring dispersant effectiveness is discussed. Mass balance is noted as necessary as otherwise losses are often interpreted as dispersant effectiveness. The paper reviews current measures and estimates the errors and mass balance errors associated with these. The paper concludes that new techniques are needed to measure the plume location and surface remaining oil, however, some suggestions are given on how current methods could be improved.

Grenon, S., and M. Boulé, "Alternative Methods in the St-Lawrence: Challenges and Decision Making Process According to the Quebec Region Working Group on Marine Spills", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 271-278, 2003.

Decision-making tools were developed for the use of in-situ burning and dispersant use along the St. Lawrence shoreline. The challenges of using this technique are also presented.

Harris, B.C., J.S. Bonner, T.J. McDonald, C.B. Fuller, C.A. Page, P. Dimitriou-Christidis, M.C. Sterling and R.L. Autenrieth, "Nutrient Effects on the Biodegradation Rates of Chemically-Dispersed Crude Oil", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 877-893, 2002.

A shake flask experiment to test the biodegradation rates of chemically-dispersed oil was carried out. It was found that biodegradation of dispersed oil fractions were nutrient-limited. Rates of biodegradation and density of the microorganisms were not affected by concentrations of the chemically-dispersed oil. Dispersed oil components biodegraded rapidly with the addition of nutrients. Microbial population densities and biodegradation rates increased when either nitrogen or phosphorus were added to the reactor except for PAH biodegradation with phosphorus

addition. The addition of nitrogen was observed to increase the biodegradation for both alkanes and PAHs. It was found that the nitrogen and phosphorus levels need to be about 10 mg/L to achieve the maximum biodegradation rate.

Harris, B.C., J.S. Bonner, T.J. McDonald, C.B. Fuller, C.A. Page, P. Dimitriou-Christidis, M.C. Sterling and R.L. Autenrieth, "Bioavailability of Chemically-Dispersed Crude Oil", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 895-905, 2002.

Shake flask experiments were conducted to evaluate the change in biodegradation rate with oil and dispersant loading. The concentration of phenanthrene, dibenzothiophene and their alkylated homologs were measured. The concentrations and disappearance of these compounds were the same at three different loadings. Thus the availability of these compounds did not affect the degradation. Further, it could be concluded that the bioavailability of these oil compounds was not increased by the use of dispersants. Variable rates of biodegradation then would have to be explained by other factors such as partitioning, temperature, nutrients or particle size.

Henry, C., "Review of Dispersant Use in U.S. Gulf of Mexico Waters since the Oil Pollution Act of 1990", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2005.

Seven spills in the Gulf of Mexico between the years of 1995 and 2005 were treated with dispersants. The history and lessons learned are given. The spills are: West Cameron 198 Pipeline spill, 1995; High Island Pipeline system Oil Spill, 1998; T/V Red Sea Gull spill, 1998; Mississippi Canyon 109 Pipeline Spill, 1998; M/V Blue Master, 1999; Poseidon Pipeline Oil Spill, 2000; and Main Pass 69 Pipeline Spill, 2004.

Hollebone, B.P., B. Fieldhouse, T. Lumley, M. Landriault, K. Doe, and P. Jackman, "Aqueous Solubility, Dispersibility and Toxicity of Biodiesels", in *Proceedings of the Thirtieth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 227-243, 2007.

Hollebone, B. P., B. Fieldhouse, M. Landriault, K. Doe, and P. Jackman, "Aqueous Solubility, Dispersibility and Toxicity of Biodiesels", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 929-936, 2008.

The physical and toxicological aspects of biodiesels were reported. Natural and chemically-enhanced dispersion of biodiesel were examined in both low- and high-energy conditions. Biodiesels were found to have significant differences with petroleum diesels in water chemistries and in potential ecological impacts. All organisms tested show that biodiesels have less acute toxicity than petroleum diesels. It remains unclear which components of the biodiesels are the most water-soluble and have the greatest potential for adverse effects on aquatic ecosystems. Neat biodiesels were found to be much more dispersible in high-energy conditions than petroleum diesel.

Ibemesim, R. "Comparative Toxicity of Two Oil Types and Two Dispersants on the Growth of a Seashore Grass, *Paspalum vaginatum* (Swartz)", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 875-880, 2008.

The effects of a heavy crude oil, light crude oil and two dispersants, Goldcrew and Corexit 9527, when used on seashore grass, *Paspalum vaginatum*. The effectiveness of removal of the oil from the plants was assessed as well as the effect on the plants. Plants treated with the heavy oil recovered after 8 days. Plant treated with the light crude oil and Corexit 9527 recorded 100% mortality. Corexit 9527 was not effective in ameliorating the effects of the light crude oil. The

recovery on the seagrass was apparent after 70 days when treated with heavy oil and Goldcrew. Both treatments resulted in lower biomass and stem density compared to the control. Plants cleaned with Goldcrew after 24 hours after oiling recovered faster than if they were treated 48 hours after. Plants exposed to the light crude or Corexit 9527 treatments did not recover.

Kaku, V.J., M.C. Boufadel and A.D. Venosa. "Evaluation of Turbulence Parameters in Laboratory Flasks Used for Dispersant Effectiveness Testing", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2005.

Two dispersant testing flasks, the swirling flask and the baffled flask, were evaluated for energy using a hot-wire anemometer. These measurements were used to compute the velocity gradient, turbulence microscale and energy dissipation rate per unit mass. The average energy dissipation rates in the swirling flask were about two orders of magnitude smaller than those in the baffled flask. The sizes of the microscales in the baffled flask were much small than that in the swirling flask and approached that thought to be in the sea.

Kepkay, P., C.W. Yeung, J.B.C. Bugden, Z. Li and K. Lee, "Ultraviolet Fluorescence Spectroscopy (UVFS)- A New Means of Determining the Effect of Chemical Dispersants on Oil Spills", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp.639-643, 2008.

The use of ultra-violet fluorescence spectroscopy to measure oil components in water is reviewed. It is suggested that this method might be used to monitor dispersant effectiveness at sea. It was noted that the emission at 445 nm is particularly enhanced by dispersants.

Khelifa, A., P.S. Hill, P. S. and K. Lee "Prediction of Oil Droplet Size Distribution in Agitated Aquatic Environments", in *Proceedings of the Twenty-Seventh Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, pp. 371-382, 2004.

A Monte Carlo model was developed to predict droplet size distribution due to Brownian motion, turbulence and differential settling. The model integrates a kinematic model to simulate droplet breakage. Simulated droplet-size distributions for a maximum size range from 19.5 to 82.5 showed good agreement with size distributions observed in the lab and field.

Khelifa, A., B. Fieldhouse, Z. Wang, C. Yang, M. Landriault, C. Brown and M. Fingas, "Effects of a Chemical Dispersant on Oil Sedimentation due to Oil-SPM Flocculation: Experiments with the NIST Standard Reference Material 1941B", in *Proceedings of The 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 627-631, 2008.

Aggregation between suspended oil droplets and suspended particulate matter (SPM), which leads to the formation of oil-SPM aggregates (OSAs), was studied to measure the size, density and settling velocity of OSAs formed. Both physically and chemically dispersed oils were considered in experiments conducted using Standard Reference Material 1941b prepared by the National Institute of Standards and Technology, Arabian Medium and South Louisiana crude oils, and Corexit 9500 chemical dispersant. No obvious effects of chemical dispersant on oil sedimentation was measured for sediment concentrations of 100 mg/L or higher. Measured oil sedimentation was 3 to 5 times higher with chemical dispersant than with physically-dispersed oil at low sediment concentrations of 25 and 50 mg/L. Measurements showed that OSAs formed with chemically-dispersed oil contain many oil droplets that are smaller than those formed from physically-dispersed oil.

Khelifa, A., C. Brown, M. Chun, and J.L.E. Eubank, "Physical Properties of Oil-SPM Aggregates: Experiments with the NIST Standard Reference Material 1941b", in *Proceedings of the Thirty-first Arctic and Marine Oil Spill*

*Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 35-51, 2008.

Aggregation between suspended oil droplets and suspended particulate matter (SPM), which leads to the formation of oil-SPM aggregates (OSAs), was studied to measure the physical properties that control the fate of OSAs. A laboratory study was conducted to measure the size, density and settling velocity of OSAs formed under various mixing conditions. Both physically and chemically dispersed oils were considered in experiments conducted using Standard Reference Material 1941b prepared by the National Institute of Standards and Technology, Arabian Medium and South Louisiana crude oils, and Corexit 9500 chemical dispersants. Two sediment-to-oil ratios of 0.5 and 1 were used. At sediment-to-oil ratio of 0.5, the results showed that oil-SPM interaction leads to formation of abundant negatively-buoyant OSAs that settle at an average rate of 1 mm/s, their average effective density is about 60 g/L and their size varies from 30 to about 350  $\mu\text{m}$ . The minimum effective density and settling velocity of OSAs measured in this study were 34 g/L and 0.3 mm/s, respectively. Slightly denser OSAs were obtained with chemically dispersed oil. Less difference was obtained between physical properties of OSAs and those of sediment flocs when the sediment-to-oil ratio was increased from 0.5 to 1. Both the Stokes' Law and a modified one overestimate the settling velocity of OSAs and are not recommended for use in oil spill modelling.

Khelifa, A., M. Fingas, B.P. Hollebone and C.E. Brown, "Effects of Chemical Dispersants on Physical Properties and Dispersion", in *Proceedings of the Thirtieth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, pp. 105-116, 2007.

Laboratory experiments were performed to measure the effects of chemical dispersants on oil physical properties and dispersion. The aims of this study were to measure the effects of dispersant-to-oil ratio (DOR) on the viscosity of crude oils, the brine-oil interfacial tension (IFT) and the related size distributions of oil droplets formed under various mixing conditions. Arabian Medium, Alaska North Slope and South Louisiana crude oils and Corexit 9500 and 9527 chemical dispersants were used to perform the study. Results showed a monotonous linear increase of oil viscosity with DOR. The increase is higher with the less viscous oils than with the more viscous oils. With increases in DOR from 0 to 1:5, oil-dispersant mixture viscosity is approximately 20, 30 and 40 % greater than the crude oils for Arabian Medium, Alaska North Slope, and South Louisiana, respectively. Similar results were obtained with both chemical dispersants. As reported in previous studies, application of chemical dispersants reduces the interfacial tension significantly for all values of DOR examined in the current study including a very low value of 1:200. For instance, the interfacial tension of Arabian Medium crude decreases from 20 mN/m to less than 3.6 mN/m (the detection limit of the instrument) at DOR=1:200. The results also show that an optimum DOR exists at which the IFT reduction reaches a maximum value. At this optimum DOR, the effectiveness of the chemical dispersant is at a maximum. The consequent effects of the observed IFT reductions on the resulting size distribution of oil droplets was studied using existing theories and size measurements using UV epifluorescence microscopy.

Kirby, M.F., B. Devoy and R.J. Law, "Ensuring the Most Appropriate Oil Spill Treatment Products are Available - A Review of Toxicity Testing and Approval Issues in the UK", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 829-833, 2008.

The UK is considering revising its dispersant approval guidelines. Issues being considered are the requirements for products to pass both effectiveness and toxicity tests, the need to approve products for specific application to oil types, the testing at lower D:O ratios, differing conditions

of temperature and salinity, and the need for a separate surface cleaner approach.

Koh, C. and F. Tan, "Dispersant Effectiveness Testing on Chemical Floaters and its Environmental Concerns", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 811-815, 2008.

Tests of oil spill dispersants on chemical slicks were assessed. Preliminary effectiveness tests on a number of chemicals were carried out and effectiveness varied from low to high percentage. Discussion on the future application of this is given.

Lambert, P., M. Goldthorp, B. Fieldhouse, Z. Wang, M. Fingas, L. Pearson, and E. Collazzi, "A Review of Oil-in-Water Monitoring Techniques: The Concluding Remarks", in *Proceedings of The 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 456-461, 2003.

A comparison study of the Turner 10AU and Turner model 10 fluorimeters was carried out by creating dispersions from two crude oils, Bunker C and a Diesel fuel using Corexit 9500. The chemical composition of the oils was determined using gas chromatographic techniques. It was found that the concentrations indicated by the fluorimeters could not be directly linked to the concentration as determined by accurate GCMS measurements. The readings could also not be correlated to sum of PAHs or individual PAHs including naphthalene, phenanthrene, etc. The discrepancies between the actual measurement and the fluorescent output could be as large as 500%.

Lambert, P., "A Literature Review on Flow-through Fluorimeters for Monitoring Oil-in-water Levels", in *Proceedings of the Twenty-seventh Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 861-880, 2004.

The results of a literature search review of fluorescence-based portable detectors to measure the real-time concentrations of oil are reported. The focus of this paper has been to summarize the literature about how the instruments were used, including set up and calibration procedures, the oil and dispersant measured, the approximate concentration range of the oil in the water column, and how the real-time data compared to traditional laboratory techniques.

Lambert, P., B. Fieldhouse, and M. Fingas, "A Discussion on the Use of Oil Spill Treating Agents in Canada", in *Proceedings of the Twenty-ninth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1077-1086, 2006.

A review of the use of treating agents, including dispersants, is given in the Canadian context. The procedures for gaining approval and for use are also summarized.

Lee, K., Z. Li, T. King, P. Kepkay, M.C. Boufadel, A.D. Venosa and J.V. Mullin, "Effects of Chemical Dispersants and Mineral Fines on Partitioning of Petroleum Hydrocarbons in Natural Seawater", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 633-638, 2008.

A flask study of oil-mineral aggregates (OMA) was carried out. It was found that chemical dispersants enhanced the transfer from the surface to the water column and promoted the formation of OMAs in the water column. Results indicated that there is not necessarily an increase in oil sedimentation when OMA formation occurs.

Li, Z., K. Lee, T. King, M.C. Boufadel and A.D. Venosa, "Oil Droplet Size Distribution as a Function of Energy Dissipation Rate in an Experimental Wave Tank", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 621-626, 2008.

A wave tank was used to conduct a study of dispersant effectiveness as a function of energy

dissipation rate for two oils and two dispersants under three different wave conditions, non-breaking waves, spilling breakers and plunging breakers. The wave tank surface energy dissipation rates were determined to be 0.005, 0.1 and 1 m<sup>2</sup>/s<sup>3</sup>. Weathered MESA and fresh ANS crudes were used. Corexit 9500 and SPC 1000 dispersant were used. High energy dissipation rates of breaking waves increased the dispersant oil concentration and reduced droplet sizes.

Lin, Q. and I.A. Mendelssohn, "Dispersants as Countermeasures in Nearshore Oil Spills for Coastal Habitat Protection", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 447-451, 2005.

A study on the use of dispersants on salt marsh plants was conducted. The tolerance of the marsh plant *Sagittaria lancifolia* to the dispersant JD-2000 was about 20 to 80 times higher than that of the standard test-organisms, *Menidia beryllina* and *Mysidopsis bahia*, respectively. The LC<sub>50</sub> of the dispersant JD-200 for *Sagittaria lancifolia* was greater than 8000 ppm. The application of the dispersant JD-2000 reduced the adverse effects of crude, diesel and number 2 fuel oil on marsh vegetation. Undispersed oil severely impacted plants. A dose of 750-ppm number 2 fuel oil resulted in more than 90% mortality for *Spartina alterniflora* in 3 weeks.

Lumley, T.C., B.P. Hollebone and S. Harrison, "Evaluation of Methods For Assessing Toxicity of Oil Spill Treating Agents", in *Proceedings of the Thirtieth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, pp. 133-150, 2007.

The toxicity of dispersants is discussed as part of Environment Canada's guidelines for their use and acceptability. Emphasis has been on evaluating toxicity by the 96-hour rainbow trout lethality test, but other toxicity tests, such as those using *Vibrio fischeri*, *Daphnia magna*, and others have also been employed. Toxicity data generated for oil spill treating agents by Environment Canada are summarized and presented in this report.

Lumley, T.C., S. Harrison and B.P. Hollebone, "Evaluation of Methods for Assessing Effectiveness of Oil Spill Treating Agents", in *Proceedings of the Thirtieth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, pp. 117-132, 2007.

This is a summary of treating agent effectiveness testing that has taken place at Environment Canada and a description of current methodologies for effectiveness testing of dispersants and other treating agents. Revision of the older guidelines is recommended in order to include updated effectiveness testing methodologies and to include testing criteria for treating agents other than dispersants.

Lyons, Z. and X. Castaneda, "The History of Dispersant Use in the U.S.", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2005.

A brief history of use, testing and approval of oil spill dispersants in the United States is given.

Martha, D., and C.N. Mulligan, "Rhamnolipid Biosurfactant Assisted Dispersion and Biodegradation of Spilled Oil on Surface Waters", Paper presented at the *2005 Proceedings, Annual Conference - Canadian Society for Civil Engineering*, 10 p. 2005.

A study of the comparison in biodegradability of oil with dispersants or biosurfactants was carried out. A Brent crude, Corexit 9500 and a biosurfactant were used. The biosurfactant, rhamnolipid is a metabolic by-product of *Pseudomonas aeruginosa*. A 25% solution of the commercial product, JBR 425, was used. The EPA biodegradation protocol using a 250 mL flask was employed. Five treatments were compared for total GCMS TPH and microbial counts over

the 35 day experiment. The treatments were oil only, chemical dispersant, bio-dispersant, a biological agent (seeded solution) and bio-dispersant with the biological agent. The most biodegradation occurred with the bio-dispersant and biological agent mixed, then the biological agent alone, then the bio-dispersant, then oil only and then finally with the dispersant only. In the measurement of microbial counts the same order was observed. It was concluded that the use of the rhamnolipid biosurfactant promoted biodegradation whereas the chemical dispersant always suppressed biodegradation.

Mearns, A., G. Watabayashi and C. O'Connor, "Using a New Dispersed Oil Model to Support Ecological Risk Assessment", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 523-530, 2003.

A mathematical model is described to assist in dispersant decisions. Trajectory maps for both chemically-dispersed and undispersed oil and concentration isopleths by depth and time are outputted. Oil isopleths are staged at concentrations and exposure times of concern as posted by experts. Two Bunker 6 fuel spill scenarios, with alternatives of dispersal or no dispersal, were developed. Two locations were chosen, one in open ocean (10,000 barrel spill) and one in an estuary (2000 barrel spill). Maximum dispersed oil concentrations were in the 10 to 20 ppm range and decreased within 24 hours to 1 to 2 ppm. Average concentrations never exceeded 3 ppm. Plankton in about 25% of the plume area were at moderate risk for 24 hours. These impacts are then compared to the no dispersion option.

Melbye, A.G., D. Altin and T. Frost, "Determination of Uptake of Dispersed Oil in Copepod *Calanus finmarchicus*", in *Proceedings of the Twenty-Fourth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 223-235, 2001.

Biological uptake of dispersed oil in the copepod, *Calanus finmarchicus*, was studied in a flow-through system. Results show that the bioaccumulation factor (BAF) was in 200 to 800 over 14 days. A large part of the hydrocarbon was adsorbed to the surface of the test organism.

Miranda, D., A. Casco and M. Moyano, "Autorización del Uso de Dispersantes en América Latina y el Caribe", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 1003-1009, 2008.

This is a review of the South American use of dispersants and the decision making process that is behind it.

Moles, A., "Juvenile Demersal Fishes: A Possible Case For the Use of Dispersants in the Subarctic", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1353-1365, 2002.

The sensitivity of certain fishes in the Alaska region are reviewed. Some of the species such as flatfish and sandlance juveniles burrow into tidal sediments. Other species such as salmon streams and herring spawning areas also are sensitive. It is suggested, that if effective, chemical dispersion might be useful to protect these juvenile demersal fishes.

Motolenich, K.M. and J.R. Clark, "Vessel Dispersant Application in Oil Spill Response", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 6 p., 2005.

Vessel dispersant application systems are reviewed. Three types of vessel application systems are noted: spray arm systems, fire monitor systems and single nozzle neat application systems. The advantages and disadvantages of each system are reviewed and methods to optimize these are given.

Mukherjee, B. and B.A. Wrenn, "Effects of Mixing Energy and Flow Dynamics on Chemical Dispersion of Crude Oil", in *Proceedings of the Thirtieth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, pp. 189-202, 2007.

Dispersion experiments were carried out in the baffled flask and paddle jar systems using dispersants at 10 and 12 HLB and at four energy dissipation rates of  $1.7 \times 10^{-4}$  to  $0.16 \text{ m}^2/\text{s}^3$ . For lower energy dissipation rates, both systems produced less than 1% dispersion of the oil. Higher energy dissipation rates produces dispersant effectiveness of 36 to 91% in the baffled flasks. Dispersion in the paddled flasks were 35 to 81% at the same energies. The droplet size distributions were bimodal in the baffled flask and trimodal in the paddle flask. The mean volume diameters were not sensitive to the energy dissipation rate.

Mukherjee, B., "Effect of Mixing Energy, Mixing Time and Settling time on Dispersion Effectiveness in Two Bench-Scale Testing Systems", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 651-656, 2008.

Dispersion experiments were carried out in the baffled flask and paddle jar systems using dispersants at 10 and 12 HLB and at four energy dissipation rates of  $4.8 \times 10^{-4}$  to  $1.6 \times 10^{-1} \text{ J/kg/s}$ . Dispersion effectiveness increased with energy dissipation to a maximum and then leveled off. In the baffled flask the maximum was 82% effectiveness, irrespective of oil/dispersant combination. In the paddled flask the maximum was either 97 or 30% depending on the dispersant used. Mixing time did not appear to affect the result - especially compared to the other variables. The droplet size distributions were trimodal in both systems. The mean volume diameters did change somewhat with the energy dissipation rate.

Mullin, J., R. Belore and K. Trudel, "Cold Water Dispersant Effectiveness Experiments Conducted at Ohmsett with Alaskan Crude Oils Using Corexit 9500 and 9527 Dispersants", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp.817-822, 2008.

This paper is a review of the testing of four Alaskan crude oils with Corexit 9527 and 9500, at the OHMSETT facility. The oils were weathered before application in the test. In the series of tests effectiveness as high as 90%, was claimed.

Nagarajan, K.R., N. Deshpande, G.A. Sorial, and J.A. Weaver, "Dispersant Effectiveness on Oil Spills - Empirical Correlations", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 801-804, 2008.

A statistical model was developed to fit baffled flask experimental data. The prime inputs to the model include oil viscosity, salinity, temperature, oil weathering and mixing energy. Four replicates of the experimental data were made and used to input to the model.

Nedwed, T., R. Belore, W. Spring and D. Blanchet, "Basin-Scale Testing of ASD Icebreaker Enhanced Chemical Dispersion of Oil Spills", in *Proceedings of the Thirtieth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, pp. 151-160, 2007.

The use of icebreakers to mix oil spill dispersions in ice conditions is discussed. Testing of this concept was carried out in a basin with ice present was carried out and shows effective dispersion occurred. The mixing extends up to 20 m below the icebreaker.

Nedwed, T., J.R. Clark, G.P. Canevari and R. Belore, "New Dispersant Delivered as a Gel", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 121-125, 2008.

A new dispersant that is a gel is described. The dispersant has up to 90% active ingredient



compared to 40 to 50 % for traditional dispersants. The concept is the buoyant gel will float and mix with the oil, rather than being washed off as many traditional dispersants. Preliminary testing with the dispersant showed that it more effective on more viscous oils and is effective at lower dispersant:oil ratios. Further, aerial application might be more successful with less drift.

Nedwed, T., and T. Coolbaugh, "Do Basins and Beakers Negatively Bias Dispersant-Effectiveness Tests", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 835-841, 2008.

The paper is a thesis on the fact that surfactant films in small-scale tests, even test tanks, surround the oil slick and keep the slicks thicker than they would normally be. Thick oil slicks require more energy to disperse. Thus, the effectiveness of these smaller scale tests give lower performance than might be expected in the open ocean.

Ojo, T., M.C. Sterling, Jr., J.S. Bonner, C.A. Page, C.B. Fuller, F. Kelly and J.C. Perez, "Field Simulation Experiment of Aerial Dispersant Application For Spill of Opportunity", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 813-824, 2003.

The paper is a review of the operation of a monitoring vessel for a field simulation of aerial dispersant application. The vessel primarily transports a fluorometer for measuring in-water oil concentrations.

Owens, C.K. and R.S. Belore, "Dispersant Effectiveness Testing in Cold Water and Brash Ice", in *Proceedings of the Twenty-Seventh Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, pp. 819-840, 2004.

Tests of the dispersion of Alaska North Slope, Hibernia and Chayvo crude oils and Corexit 9527 were carried out in 3-m diameter circles in the OHMSETT tank. Ice blocks and ice chips were placed in the circles to simulate 0/10, 4/10 and 8/10 ice coverages. The amount of dispersion was observed for waves of 17 cm and 33 cm heights with 4 and 5.5 second periods. It was observed that the ice enhanced the apparent dispersion and much of the oil appeared to be dispersed. With weathered crudes, dispersion was observed to be less.

Page, C., J. Bonner, C. Fuller and M. Sterling, "Dispersant Effectiveness in a Simulated Shallow Embayment", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 721-733, 2002.

An experiment in the SERF facility in Corpus Christi was carried out to assess the dispersant effectiveness of a weathered Arabian medium crude and Corexit 9500. The effectiveness was measured by conducting a mass balance on the oil where the compartments included the water column, the water surface and the tank walls. Samples were periodically collected from each compartment at 0.5, 2, 4 and 24 hours. At the 4-hour point about 2/3 of the oil was in the water column. After 24 hours, a large portion of the oil had re-surfaced.

Payne, J.R., E. Terrill, M. Carter, M. Owens, W. Middleton, A. Chen, D. French-McCay, C. Mueller, K. Jayko, W. Nordhausen, R. Lewis, M. Lampinen, T. Evans, C. Ohlmann, G.L. Via, H. Ruiz-Santana, M. Maly, B. Willoughby, et al. "Evaluation of Field-collected Drifter and Subsurface Fluorescein Dye Concentration Data and Comparisons to High Frequency Radar Surface Current Mapping Data for Dispersed Oil Transport Modeling. in *Proceedings of the Thirtieth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 681-712, 2007.

Payne, J.R., E. Terrill, M. Carter, M. Owens, W. Middleton, A. Chen, D. French-McCay, C. Mueller, K. Jayko, W. Nordhausen, R. Lewis, M. Lampinen, T. Evans, C. Ohlmann, G.L. Via, H. Ruiz-Santana, M. Maly, B. Willoughby,

C. Varela, P. Lynch, and P. Sanchez, "Field Measurements of Fluorescein Dye Dispersion to Inform Dispersed-Oil Plume Sampling and Provide Input for Oil-Transport Modeling", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 515-525, 2008.

Fluorescein dye experiments, HF radar, drogue tracking and extensive documentation were carried out off California near San Diego to predict the movement of dispersed oil. The mixed layer depth and other critical parameters were determined for input into spill models and subsequently into the decision-making process.

Payne, J.R. and A.A. Allen, "Use of Natural Oil Seeps For Evaluation of Dispersant Application and Monitoring Techniques", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 241-245, 2005.

Laboratory tests with the seep oil were conducted. Results from those tests indicated that the 11° API gravity seep oil from the Monterey Formation was not amenable to treatment with dispersants (0% dispersion), but similar tests on nearby Platform Holly produced oil (also from the Monterey Formation) indicated a possible dispersion of up to 70%. A limited set of *in situ* field tests (using a hand-held spray bottle with less than one pint of Corexit 9500) were completed on the seep oils in June 2003 to determine if the earlier laboratory results were an artifact of the seep oil collection and shipment or some other unknown factor. The field tests convincingly demonstrated that the natural seep oils were not amenable to treatment with Corexit 9500.

Ramachandran, S.D., P.V. Hodson, C.W. Khan and K. Lee, "PAH Uptake by Juvenile Rainbow Trout Exposed to Dispersed Crude Oil", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 743-753, 2003.

This was an experiment to measure whether oil dispersion increases or decreases the exposure of aquatic species to the toxic components of oil. To evaluate whether fish would be exposed to more polycyclic aromatic hydrocarbon (PAH) in dispersed oil relative to equivalent amounts of the water-accommodated fraction (WAF), measurements were made of CYP1A induction in trout exposed to the dispersant, Corexit 9500, WAFs, and the chemically enhanced WAF (dispersant; CEWAF) of three crude oils. The crude oils comprised the higher viscosity Mesa and Terra Nova and the less viscous Scotian Light. Total petroleum hydrocarbon and PAH concentrations in the test media were determined to relate the observed CYP1A induction in trout to dissolved fractions of the crude oil. CYP1A induction was 6- to 1100-fold higher in CEWAF treatments than in WAF treatments, with Terra Nova having the greatest increase, followed by Mesa and Scotian Light. Mesa had the highest induction potential with the lowest EC<sub>50</sub> values for both WAF and CEWAF. The dispersant Corexit was not an inducer and it did not appear to affect the permeability of the gill surface to known inducers such as  $\beta$ -naphthoflavone. These experiments suggest that the use of oil dispersants will increase the exposure of fish to hydrocarbons in crude oil.

Ramachandran, S. D., C.W. Khan, P.V. Hodson, K. Lee, and T. King, "Role of Droplets in Promoting Uptake of PAHs by Fish Exposed to Chemically Dispersed Crude Oil", in *Proceedings of the Twenty-seventh Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 765-772, 2004.

Fish were exposed to the water-accommodated fraction (WAF), exposed to the dispersant, Corexit 9500, WAFs, benzopyrene and the chemically enhanced WAF (dispersant; CEWAF) of crude oils. Gills were examined by epifluorescence to determine whether the exposure was by dissolved components or by droplets directly. Chemical analysis of gills and livers were carried out to determine the exact exposures of the fish to the PAHs. Data shows that whole oil was also

taken up and thus oil was taken up by fish by both droplets and by adsorption of components through the gills.

Rubini, K., “Developing a Comprehensive International Curriculum in Oil Spill Dispersant Operations”, in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2005.

A proposed operations and training curriculum is presented to provide for dispersant operations.

Salt, D., R. Stockham, and S. Byers, “Technical Innovation in Light Aircraft Dispersant Application Systems”, in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 4 p., 2003.

New strategies for the deployment of dispersants using aircraft are reviewed. The development of alternative small-aircraft packages are summarized.

Schmidt-Etkin, D. S., D. French-McCay, J. Rowe, N. Whittier, S. Sankaranarayanan, and L. Pilkey-Jarvis, “Impacts of Response Method and Capability on Oil Spill Costs and Damages for Washington State Spill Scenarios”, *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 7 p., 2005.

Initial modeling showed little difference in costs and impacts between various on-water response options, other than that the no-response option showed higher costs because of the large shoreline impacts. With adjustment to lower theoretical oil recovery efficiencies, the model showed much greater differentials between different countermeasures options.

Schmidt-Etkin, D., “Financial Implications of Hypothetical San Francisco Bay Oil Spill Scenarios- Response, Socioeconomic, and Natural Resource Damage Costs”, in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 9 p., 2003.

Modeling of potential spills in San Francisco Bay shows that the Natural Resource Damage Assessment (NRDA) costs are much less than previously thought. The hypothetical estimates also show that effective dispersant application could significantly reduce the overall costs by reducing response costs and NRDA costs.

Schmidt-Etkin, D. and P. Tebeau, “Assessing Progress and Benefits of Oil Spill Response Technology Development since EXXON VALDEZ”, in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 8 p., 2003.

Progress is stated to have been made in the three major areas of spill countermeasures including mechanical, dispersants and in-situ burning. Future scenarios vary in their ability to predict effects of improvements in these countermeasures. Thus, the old spills are used to demonstrate the cost-effectiveness of developments in these areas.

Simecek-Beatty, D., C. O'Connor and W.J. Lehr, “3-D Modelling of Chemically Dispersed Oil”, in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1149-1159, 2002.

The paper describes the development of a 3-D modeling capability to add dispersant plumes to the existing GNOME model. The equations are presented and discussed.

Simmons, M., “The MSC NAPOLI Incident”, in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 1063-1066, 2008.

The incident of the NAPOLI is described and the limited dispersant application carried out on that incident. The main focus of this incident was the recovery of shipping containers.

Spring, W., T. Nedwed and R. Belore, "Icebreaker Enhanced Chemical Dispersion of Oil Spills", in *Proceedings of the Twenty-Ninth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, pp. 711-727, 2006.

Laboratory and scaled tank tests of mixing by azimuthal-stern-drive ice breakers to disperse oil spills were carried out. The scaled tests showed effective dispersion, even on weathered oils.

Steen, A. and A. Findlay, "Frequency of Dispersant Use Worldwide", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 645-649, 2008.

A review of the published literature on dispersant use around the world shows 213 documented uses since 1968 and 38 in the last decade. Overall, about 50% of the events were noted as being effective and the other half about equally ineffective or inconclusive, or undocumented. Use is now highest in Africa and Asia. The reporting of use is noted as inconsistent and in some cases, absent.

Sterling, M.C., Jr., T. Ojo, R.L. Autenrieth, J.S. Bonner, C.A. Page and A.N.S. Ernest, "Coalescence Kinetics of Dispersed Crude Oil in a Laboratory Reactor", in *Proceedings of the Twenty-Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 741-753, 2002.

Coalescence kinetics of premixed crude oil and chemical dispersant were determined within a range of mean shear rates ( $Gm^{-1/2}$  5, 10, 15, 20  $s^{-1}$ ) and salinity (10‰, 30‰) values. A controlled shear batch reactor was created in which the coagulation of dispersed oil droplets was monitored in-situ. The combination of a particle counter and an in-situ laser scattering instrument provided analysis of droplet size distributions and dispersed droplet mass. Coalescence reaction rates were modeled using Smoluchowski reaction kinetics. Measured collision efficiency values ( $\alpha = 0.25$ ) suggest insignificant resistance to coalescence in shear systems. Experimentally determined dispersant efficiencies were 10–50% lower than that predicted using a non-interacting droplet model.

Sterling, M.C., R.L. Autenrieth, J.S. Bonner, C.B. Fuller, C.A. Page, T. Ojo and A.N.S. Ernest, "Dispersant Effectiveness and Toxicity: An Integrated Approach", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 335-339, 2003.

Using a dual-process view of dispersion, dispersant-slick mixing and transport into the water column, a new description is given. Using a drop coalescence model, the droplet coalescence rates of dispersed oil were determined. Experimental dispersion efficiencies and droplet size distributions were compared to those predicted by Stokes resurfacing. Experimental dispersion efficiency values decreased linearly with increased mean shear rates due to increased coalescence rates. Increased droplet coalescence in the water column adversely impacts overall dispersant efficiency. A toxicity evaluation chamber was attached directly to the physical measurement chamber. Toxicity was then related directly to the droplet size and mass. The 96-hour mortality of *Menidia beryllina* varied from 2% (no dispersant) to 87% (dispersed oil).

Sterling, M.C., Jr., T. Ojo, R.L. Autenrieth, J.S. Bonner, C.A. Page and A.N.S. Ernest, "Application of Particle Population Kinetics in Modelling the Vertical Transport of Chemically Dispersed Crude Oil", in *Proceedings of the Twenty-Sixth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 787-798, 2003.

A model is developed to predict the influence of coalescence on the resurfacing of oil

droplets. Dispersed oil droplets were separated into size classes and the transport of each was modeled using an advection-dispersion-reaction equation. The coalescence was described using Smoluchowski aggregation kinetics. If coalescence was removed, resurfacing is reduced by 35 to 40%. Decreasing droplet concentrations also decreased resurfacing by 25%. Changing shear rate also resulted in a 50% change in resurfacing rate.

Stevens, L. and J. Roberts, "Dispersant Effectiveness on Heavy Fuel Oil and Crude Oil in New Zealand", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 509-513, 2003.

The Warren Springs test was used to test the effectiveness of New Zealand stocked dispersants, Corexit 9527, Slickgone, Gamlen, and Tergo. Effectiveness was considered to be values greater than 15%. Seven crude oils and two fuel oils were tested. All dispersants appeared to be successful on all the crude oils. The IFO-380 was not dispersible by this test.

Stone, T., "The UK Response to the NAPOLI Incident", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 1037-1042, 2008.

The incident of the NAPOLI is described and the limited dispersant application carried out on that incident. The main focus of this incident was the recovery of shipping containers.

Taylor, E., M. Hodges, A. Steen, D. Miranda, M. Meza, J. Ramos, B. Couzigou and M. Moyano, "IOSC Workshop Report- A Proposed International Guide for Oil Spill Response Planning and Readiness Assessment", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 1-17, 2008.

This paper reports on a series of workshops intended to advance international practices and approaches to the decision-making for oil spill response. The plan identifies a number of elements which are to be included in any national approach and defines what would be included in the elements.

Trudel, K., S. Ross, R. Belore, S. Buffington, G. Rainey, C. Ogawa and D. Panzer, "Technical Assessment of Using Dispersants on Marine Oil Spills in the U.S. Gulf of Mexico and California", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 515-522, 2003.

This is an assessment of the operational and environmental issues associated with dispersant use on federal OCS facilities in the Gulf of Mexico and California. The dispersability of the GOM oils is examined and it is concluded that most are dispersible. The Pacific oils on the other hand, are not dispersible. The capabilities of spray platforms are examined and a net environmental benefit analysis is presented.

Trudel, K., S.L. Ross, R. Belore, S. Buffington and G. Rainey, "Technology Assessment of the Use of Dispersants on Spills From Drilling and Production Facilities in the Gulf of Mexico Outer Continental Shelf", in *Proceedings of the Twenty-Fourth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 531-549, 2001.

This is an assessment of the operational and environmental issues associated with dispersant use on federal OCS facilities in the Gulf of Mexico. The dispersability of the oils is examined and it is concluded that most are dispersible. The capabilities of spray platforms are examined and a net environmental benefit analysis is presented.

Trudel, B.K., R.C. Belore, A. Lewis, A. Guarino and J. Mullin, "Determining the Viscosity Limits For Effective Chemical Dispersion: Relating OHMSETT Results to Those From Tests At-Sea", in *Proceedings of the 2005 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 71-76, 2005.

This reports on a comparison between at-sea tests of IFO-180 and IFO-380 and those conducted at OHMSETT. The at-sea tests suggested a viscosity limit for dispersion at low wave energy (winds 7 to 14 knots) was between the 2075 and 380 cP of the two oils. At higher sea energy this limit would be higher. These tests suggest that there is not a single value of viscosity as the limitation, but rather a range depending on wave energy and dispersant type.

Venosa, A.D., K. Lee, M. Boufadel, Z. Li, W. Wickley-Olsen, and T. King, "Dispersant Effectiveness as a Function of Energy Dissipation Rate in an Experimental Wave Tank", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 777-783, 2008.

A test tank was used to compare the dispersion rate of dispersed and undispersed oil at various energy dissipation rates. Three wave conditions were used, regular non-breaking waves, spilling breakers and plunging breakers. Dispersion amounts increased considerably with the addition of dispersants and with increasing energy dissipation rates.

Vik, A.M., "New Norwegian Policy on use of Dispersants", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 2 p., 2003.

The Norwegian policy on dispersants is set out. Dispersant use will be considered, but a thorough analysis must be done in advance and the criteria for use be documented in a contingency plan. The use of dispersants is prohibited unless well-planned and executed. Applications to the government must precede use.

Ward, G.A., B. Baca, W. Cyriacks, R.E. Dodge and A. Knap, "Continuing Long-Term Studies of the Tropics Panama Oil and Dispersed Oil Spill Sites", in *Proceedings of the 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 259-267, 2003.

The experiment, TROPICS - Tropical Oil Pollution Investigations in Coastal Systems, was reviewed. The experiment involved the deposition of non-treated Prudhoe Bay crude oil and dispersant oil into two separate sites, dominated by nearshore mangrove, seagrass and coral systems in the year 1984. The site was monitored and analyzed after 30 days, 3 months, 2, 6, 10, 17, and 18 years. Oil caused mortality in the short term to invertebrate fauna, seagrass beds, and corals at both the oil and unoiled sites. This was compared to an unoiled site. At the untreated site there was some mortality to the mangroves in the first period of time. The oiled site shows an invasion of finger coral and the coverage has grown from 33 to 37 % over the 18 year period.

Weng, H.Y., "Oil Spill Responses - The Political Dimension", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 587-590, 2008.

A review of oil spill response internationally is given. Focus is on the problems of coordinating response given the political dimension such as roadblocks thrown up such as refusal to participate in exercises because of 'security' concerns.

Wickley-Olsen, E., M.C. Boufadel, T. King, Z. Li, K. Lee and A.D. Venosa, "Regular and Breaking Waves in Wave Tank for Dispersion Effectiveness Testing", in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 499-508, 2008.

The energy dissipation rate in a test tank was measured for regular and two types of breaking waves. The plunging breaking waves had heights of 0.25 m. Breaking waves decreased in energy from  $1 \cdot 10^{-2}$  watt/kg just below the surface to  $5 \cdot 10^{-4}$  watt/kg 20 cm deep in the water column. Regular waves had only an energy dissipation rate of  $5 \cdot 10^{-6}$  in the water column.

Yender, R., K. Stanzel, and A. Lloyd, "Impacts and Response Challenges of the Tanker SOLAR 1 Oil Spill,

Guimaras, Philippines- Observations of International Advisors”, in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 77-81, 2008.

This is a review of the impact and response of the Solar I oil spill in the Philippines. Although dispersants were discussed, they were not used. Recovery after physical recovery is proceeding well in the affected areas, including mangroves.

### 6.3 ‘Gray’ Literature (not formally peer-reviewed)

AFF, *The Approval and Use of Oil Dispersants in the UK*, Ministry of Agriculture, Fisheries and Food, Great Britain, London, <http://www.defra.gov.uk/environment/water/marine/uk/oilspill/dispersants.pdf>, 46 p., 2006.

This is the public description of the laws in the United Kingdom that set out the use of oil spill dispersants. Dispersants can be used on spills given that the product is approved, that the water depth is greater than 20 m and that the relevant authorities approve that use. The licensing authority may approve use in waters of depth less than 20 m.

ASTM, 1413, *Standard Guide for Oil Spill Dispersant Application Equipment: Boom and Nozzle Systems*, American Society for Testing and Materials, West Conshohocken, PA, 2004.

This standard covers the design of boom and nozzle dispersant application systems intended either for vessels or aircraft. Minimum equipment requirements such as the presence of flow and pressure meters are noted. The design equations for the nozzles, discharge rate and applied pressure are given separately for aircraft and vessels systems. Basic material requirements are noted. The required information to be supplied to the user is specified.

ASTM, 2059, *Standard Test Method for Laboratory Oil Spill Dispersant Effectiveness Using the Swirling Flask*, American Society for Testing and Materials, West Conshohocken, PA, 2006.

This standard covers the testing of dispersant effectiveness using the swirling flask method. Standard materials, reagents and procedures are specified. The vessel used is prescribed and the procedures used to take samples. The analytical method is specified to be gas chromatography - flame ionization detection and this method is provided. Procedures for calibrating the method and calculating the effectiveness are given.

ASTM, 2532, *Guide for Determining the Net Environmental Benefits of Dispersant Use*, American Society for Testing and Materials, West Conshohocken, PA, 2006.

The use of Net Environmental Benefits (NEBA) for dispersants is summarized. An example of how NEBA would be developed is given.

ASTM, 1460, *Calibrating Oil Spill Dispersant Application Equipment Boom and Nozzle Systems*, American Society for Testing and Materials, West Conshohocken, PA, 2007.

Boom and nozzle systems require ‘calibration’, that is verification of flow rates, tank capacities and nozzle operation. Equipment needed is specified. Procedures to carry out and document the procedures for this calibration are given.

ASTM, 1737, *Use of Oil Spill Dispersant Application Equipment During Spill Response: Boom and Nozzle Systems*, American Society for Testing and Materials, West Conshohocken, PA, 2007.

The use of boom and nozzle systems, vessel or aircraft-mounted is described. Specifications

on mounting and operational modes are given. The use of observers is specified for aircraft operations. Requirements for logistic and material support are given. Types of slicks and dispersant application rates are noted.

ASTM, 1738, Standard Test Method for Determination of Deposition of Aerially Applied Oil Spill Dispersants, American Society for Testing and Materials, West Conshohocken, PA, 2007.

Three alternative methods to determine the deposition amounts and patterns from aerial application of dispersants, is given. Methods of measure droplet size are described. The calculation methods and errors are summarized.

ASTM, 2205, Ecological Considerations for the Use of Chemical Dispersants in Oil Spill Response: Tropical Environments, American Society for Testing and Materials, West Conshohocken, PA, 2007.

Considerations for dispersant use in tropical regions are presented. A summary of the effects of oil and dispersed oil on tropical environments and biota is given. Recommendations are given that the receiving environment must be considered to decide on dispersant application. Dispersant use decisions should include consideration of the proximity of the dispersant application to sensitive marine environments including mangrove forests, seagrasses and corals.

ASTM, 2465, Standard Guide for Oil Spill Dispersant Application Equipment: Single-point Spray Systems, American Society for Testing and Materials, West Conshohocken, PA, 2007.

This standard covers the specification of single-point dispersant application systems intended for vessels. Minimum equipment requirements such as the presence of flow and pressure meters are noted. The design requirements for the nozzle, discharge rate and deposition are given. Basic material requirements are noted. The required information to be supplied to the user is specified.

ASTM, 1209, Ecological Considerations for the Use of Oilspill Dispersants in Freshwater and Other Inland Environments, Ponds and Sloughs, American Society for Testing and Materials, West Conshohocken, PA, 2008.

Considerations for dispersant use on sloughs or ponds are presented. A summary of the effects of oil and dispersed oil on ponds and sloughs and biota are given. Recommendations are given that the receiving environment must be considered to decide on dispersant application. A NEBA analysis should be performed before application.

ASTM, 1210, Ecological Considerations for the Use of Oilspill Dispersants in Freshwater and Other Inland Environments, Lakes and Large Water Bodies, American Society for Testing and Materials, West Conshohocken, PA, 2008.

Considerations for dispersant use on lakes are presented. A summary of the effects of oil and dispersed oil on lakes and biota typically found near lakes, is given. Recommendations are given that the receiving environment must be considered to decide on dispersant application. A NEBA analysis should be performed before application. The use of dispersants near water intakes is not recommended because there is a possibility of inducing contamination.

ASTM, 1231, Ecological Considerations for the Use of Oilspill Dispersants in Freshwater and Other Inland Environments, Rivers and Creeks, American Society for Testing and Materials, West Conshohocken, PA, 2008.

Considerations for dispersant use on rivers or creeks are presented. A summary of the effects of oil and dispersed oil on rivers or creeks and biota typically found near them, is given. Recommendations are given that the receiving environment must be considered to decide on dispersant application. A NEBA analysis should be performed before application. The use of dispersants near water intakes is not recommended because there is a possibility of inducing



contamination

ASTM, 1279, Ecological Considerations for the Restriction of the Use of Surface Washing Agents: Permeable Land Surfaces, American Society for Testing and Materials, West Conshohocken, PA, 2008.

The use of surfactant-containing treating agents is not recommended on any land surface that is permeable. Damage to the subsurface and groundwater is likely.

ASTM, 1280, Ecological Considerations for the Use of Oilspill Dispersants in Freshwater and Other Inland Environments, Impermeable Surfaces, American Society for Testing and Materials, West Conshohocken, PA, 2008.

Recommendations are given that the receiving environment must be considered to decide on dispersant application. A NEBA analysis should be performed before application.

Aurand, D., and G. Coehlo, "Ecological Risk Assessment Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Mexico – United States Pacific Coastal Border Region" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 06-02, <http://www.ecosystem-management.net/c/7/project-reports>, 50 p., 2006.

This paper reports on a workshop to evaluate the relative risk to natural resources from various oil spill response options (on-water mechanical recovery, dispersant application, and on-shore mechanical recovery) compared to natural recovery, which in the context of the workshops refers to oil removal by natural processes only. The spill scenario involved a release of approximately 70,000 gallons of Intermediate Fuel Oil (IFO) due to an accident five nautical miles west of Point Loma, CA. The workshop involved participants from both the United States (US) and Mexico, and was designed to emphasize cooperative decision-making when a spill in US waters threatened shoreline resources in both countries and when consideration of dispersants would lead to increased risk to valuable offshore resources in Mexican waters. The participants concluded that on-water mechanical recovery, in this scenario, was unlikely to be effective in reducing shoreline impacts. While dispersants offered some benefits to the shoreline, the groups did not agree as to the magnitude. All groups concluded that protection of the Tijuana Slough was a high priority, and that the current strategy of placing a berm across the entrance to prevent contamination was a critical element of the response plan. If this was not successful cleanup would be very difficult, if not impossible. Environmental concerns were largely driven by the risk to sea birds, and secondarily to intertidal invertebrates. When dispersants were used, there was an increased risk to sensitive offshore habitats and water column resources, especially around the Coronado Islands.

Aurand, D., and L. Walko, "Ecological Risk Assessment Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Casco Bay, Maine" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 03-02, <http://www.ecosystem-management.net/c/7/project-reports>, 36 p., 2003.

This paper also reports on a workshop to evaluate the relative risk to natural resources from various oil spill response options (on-water mechanical recovery, dispersant application, and shoreline removal) compared to natural recovery. The spill scenario involved a release of approximately 1,200 barrels (50,000 gallons) of Brent crude near the southern edge of Casco Bay, under conditions which threatened some interior islands and some exterior coastline. At the conclusion of the workshop, participants developed lessons learned along with recommendations for the Regional Response Team (RRT) and local Area Committee to improve local response planning efforts.

Aurand, D., and G. Coehlo, "Ecological Risk Assessment Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Delaware Bay" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 06-01, <http://www.ecosystem-management.net/c/7/project-reports>, 56 p., 2006.

This paper also reports on a workshop whose purpose was twofold: First, in response to the M/V Athos 1 oil spill in November 2004 and the ongoing work of the Area Committee, the USCG sought to bring together the various non-spill response resource managers and scientists in the Delaware Estuary. The workshop allowed the participants the opportunity to evaluate the relative risk to natural resources from various oil spill response options (on-water mechanical recovery, dispersant application, and on-shore mechanical recovery) compared to natural recovery. The spill scenario involved a release of approximately 60,000 gallons of Nigerian Qua Iboe crude oil due to an accident in the main channel of the upper estuary. The scenario times period was selected to incorporate possible impacts to signature estuary species. During this period of time large populations of migratory shorebirds would be present in the estuary and Horseshoe Crab spawning would be occurring.

After evaluating the various spill response options within the parameters presented for this scenario the groups came to the consensus that the most benefit to the environment occurred with dispersant use, if the dispersant application was highly effective (85% removal). However, the groups questioned how realistic this scenario would be considering all the variables affecting a dispersant's effectiveness, e.g., weather, temperature, sea state, spill product, logistics of dispersal, time constraints, dispersant availability and supply, water depth, circulation patterns and flushing rates, natural resources, etc. When considering a more realistic effectiveness ranges within 35-50% the benefits of dispersant use, in this ERA Consensus Workshop – Delaware Bay 2 scenario, are not dramatic as the original 85% effectiveness rating.

Primary risks noted by all groups, to shore birds, waterfowl and Horseshoe Crabs on the water surface and along the shoreline, were all reduced in that case. Concerns were voiced regarding the increase over exposure of water column organisms to dispersed oil. This concern was less than the risk perceived to the other resources.

Aurand, D. "Ecological Risk Assessment: Consensus Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Santa Barbara Channel" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 02-01, <http://www.ecosystem-management.net/c/7/project-reports>, 27 p., 2003.

In March and April of 2002, Regional Response Team (RRT) IX sponsored a workshop to evaluate the relative risk to natural resources from various oil spill response options (onwater mechanical recovery and dispersant application) in comparison to natural recovery. The spill scenario involved the release of 10,000 barrels of Intermediate Fuel Oil (IFO) 180 in the northern end of the Santa Barbara Channel, under conditions which threatened the interior coastline of the Channel Islands. The workshop involved two meetings during which participants received briefings on the expected results of the spill with and without response options, the relative effectiveness of on-water mechanical recovery, dispersants and on-water in situ burning, and the risks and benefits of these response options to the habitats and natural resources of the area. The participants were then divided into three focus groups and were asked to develop relative risk scores for the various alternatives, using standard analytical protocols outlined in the Coast Guard guidebook entitled "Developing Consensus Ecological Risk Assessments: Environmental Protection in Oil Spill Response Planning. A Guidebook." The scores from the three groups were then compared and a composite risk matrix developed which represented the overall consensus of the entire group. At the conclusion of the second meeting, the group developed a list of lessons

learned and recommendations for the RRT and local Area Committee which they felt would improve local response planning efforts.

Aurand, D., "Ecological Risk Assessment: Consensus Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Maryland Eastern Shore" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 02-02, <http://www.ecosystem-management.net/c/7/project-reports>, 42 p., 2003.

In June and July of 2002, U.S. Coast Guard sponsored a workshop to evaluate the relative risk to natural resources from various oil spill response options (on-water mechanical recovery with shoreline protection, on-shore in situ burning, on-shore mechanical recovery and dispersant application) in comparison to natural recovery. The spill scenario involved the release of 2,000 barrels of Number 6 Fuel Oil near the north end of Kent Island in Tolchester Channel under conditions which threatened the Eastern Shore of the Chesapeake Bay in the vicinity of the Eastern Neck Wildlife Refuge. Specific recommendations on future discussions were made.

Aurand, D., and G. Coehlo, "Ecological Risk Assessment Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Guayanilla Bay Area, Puerto Rico" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 07-01, <http://www.ecosystem-management.net/c/7/project-reports>, 61 p., 2007.

In February/March 2007, the United States Coast Guard (USCG) Sector San Juan sponsored a workshop to provide training in dispersant use in oil spills and to evaluate the relative risk to natural resources from various oil spill response options including no response (natural recovery), on-water mechanical recovery, dispersant application and on-shore mechanical recovery. The spill scenario was designed to present the participants with a situation where nearshore coral reefs and sea grass beds, as well as mangrove forests, were at risk. According to the scenario, a tanker carrying 100,000 barrels of Venezuelan Recon crude oil went hard aground on a reef at the entrance to Guayanilla Harbor, Puerto Rico and had two releases of oil, the first of 4000 barrels, and the second an additional 10,000 barrels (approximately 48 hours later). A total of 14000 bbls, or 588,000 gallons, was released over the 2-day and 6 hour period. The groups concluded that, because of the size of the spill, there were serious risks to both shoreline and shallow water habitats. On-water mechanical recovery was viewed as being of limited utility in this scenario. Dispersant use raised serious concerns because of the large volume of dispersed oil but did provide some benefit to shoreline and intertidal habitats. Likewise, on-shore mechanical recovery was beneficial to some habitats, but raised serious concerns in mangrove areas. The size of the spill made it unlikely that any alternative would be effective in preventing serious impacts.

Aurand, D., and G. Coehlo, "Ecological Risk Assessment Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Mexico– United States Gulf of Mexico Coastal Border Region" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 07-04, <http://www.ecosystem-management.net/c/7/project-reports>, 64 p., 2007

In October/November 2007, the United States Coast Guard (USCG) Sector Corpus Christi hosted a workshop to provide training in dispersant use in oil spills and to evaluate the relative risk to natural resources from various oil spill response options including no response (natural recovery), on-water mechanical recovery, dispersant application and on-shore mechanical recovery. The workshop involved participants from both the United States (US) and Mexico, and was designed to emphasize cooperative decision-making when a spill threatens shoreline resources in both countries. The spill scenario was designed to present participants a situation with similar threats and decisions on both sides of the US-Mexico border. In the scenario, oil spilled approximately 3 miles offshore and the potential response actions were evaluated to

determine their influence on the impact of the spill on sensitive coastal and estuarine resources. According to the scenario, after an explosion in the engine room, a tanker carrying 1.2 million gallons of Angola Soyo Crude Oil had two releases of oil. The first spill of 60,000 gallons was expected to come ashore primarily in the US, and, approximately 42 hours later, a second spill released an additional 80,000 gallons of oil expected to come ashore in Mexico. After evaluating the options within the parameters presented for this scenario, the groups concluded that because of the size of the spill, there were potential serious risks to both shoreline and shallow water habitats. On-water mechanical recovery was viewed as being of limited utility in this scenario. Dispersant use raised serious concerns but did provide some benefit to shoreline and intertidal habitats. Likewise, on-shore mechanical recovery was beneficial to some habitats, but raised serious concerns in mangrove areas. The size of the spill made it unlikely that any alternative response would be effective in preventing serious impacts. The highest concern was for estuarine habitats.

Aurand, D., and G. Coehlo, "Ecological Risk Assessment Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Cape Flattery, Washington" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 05-01, <http://www.ecosystem-management.net/c/7/project-reports>, 32 p., 2006.

Between January and November, 2005 Regional Response Team (RRT) X sponsored three workshops to evaluate the relative risk to natural resources from an oil spill off the straits of Juan de Fuca which threatened the northwest coast of Washington. The primary purpose of the workshops was to increase understanding of the overall risk, and the role different response technologies might play in mitigating that risk, relative to other response options. The participants did not feel that there was sufficient consensus on the risk ranking process to publish the results.

Aurand, D., and G. Coehlo, "Ecological Risk Assessment: Consensus Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. Upper Florida Keys" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 02-03, <http://www.ecosystem-management.net/c/7/project-reports>, 42 p., 2003.

In late August 2002, the United States Coast Guard (USCG) District 7 sponsored a workshop to discuss the relative risks to natural resources from various oil spill response options (on-water mechanical recovery, dispersant application and to a lesser extent, shoreline protection) in comparison to natural recovery. These discussions were based on a spill scenario involving the release of 100,000 gallons of Intermediate Fuel Oil (IFO) 180 near Molasses Reef in the Florida Keys, under conditions which threatened mainland shoreline habitats, a number of offshore islands, and a variety of valuable subtidal habitats. After participants received briefings on the expected results of the spill with and without response options, the relative effectiveness of two options, on-water mechanical recovery and dispersants, was evaluated. After the primary scenario was examined, two additional scenarios (one near the entrance of Biscayne Bay and one near Looe Key) were evaluated to examine the general applicability of the discussions for the Molasses Reef scenario. In general, participants concluded that on-water mechanical recovery, in the scenario under consideration, was unlikely to provide much protection for shoreline habitats. Dispersant use, if effective, did provide such protection, but with some increased risk to coral habitat in shallow water (less than 5 meters). This risk did not extend to deeper habitats.

Aurand, D., and G. Coehlo, "Ecological Risk Assessment Workshop: Environmental Tradeoffs Associated With Oil Spill Response Technologies. U.S. and British Virgin Islands" Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 03-03, <http://www.ecosystem-management.net/c/7/project-reports>, 34 p., 2003.

In mid-June 2003, the United States Coast Guard sponsored a workshop to provide oil spill response training based on the relative risk to natural resources from various oil spill response options (on-water mechanical recovery, dispersant application and shoreline cleanup) in comparison to natural recovery. The discussions were based on a spill scenario involving the release of 5,000 barrels (210,000 gallons) of Venezuelan crude oil (Furrial) approximately five miles north of Virgin Gorda Island, under conditions which threatened the coastline of several islands, as well as a variety of valuable sub-tidal habitats. In general, participants concluded that on-water mechanical recovery was unlikely to provide much protection for shoreline habitats in the scenario under consideration. Dispersant use, if effective, did provide such protection, but with some increased risk to coral habitat. This risk was limited because much of the area where dispersants were applied was relatively deep.

Aurand, D. and G. Coehlo (Editors) "Cooperative Aquatic Toxicity Testing of Dispersed Oil and the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF)." Ecosystem Management & Associates, Inc. Lusby, MD. Technical Report 05-03, <http://www.ecosystem-management.net/c/7/project-reports>, 105 p., 2005.

This report summarizes the goals, results, and conclusions of a cooperative program to improve the knowledge base related to the toxicity and environmental effects of dispersants and dispersed oil when dispersants are used in oil spill response. It contains results for three toxicity testing programs co-funded by the American Petroleum Institute and the California Office of Oil Spill Prevention and Response, the Texas General Land Office, and the Florida Department of Environmental Protection. This program was known as the "Chemical Response to Oil Spills: Ecological Research Forum," or CROSERF. The purpose of CROSERF was to provide state, federal, and international agencies, industry, academic researchers and consultants engaged in research on the ecological effects of oil spill response chemicals, especially dispersants, with a forum for the exchange of ideas and coordination of research. Specific objectives of the Forum included: • Discuss and resolve scientific issues related to ecological effects of chemicals used in oil spill response • Encourage the standardization of laboratory toxicity test procedures • Foster cooperative laboratory and mesocosm ecological research programs on oil spill response issues of mutual interest • Encourage the application of appropriate laboratory data collected under realistic exposure scenarios to the oil spill response decision process • Contribute to the development of appropriate risk assessment protocols.

One of the critical issues in the interpretation of laboratory toxicity data for dispersants and dispersed oil is the lack of standard protocols. As one of the main objectives of this program, the laboratory researchers spent considerable effort evaluating ways to improve such tests, and ultimately developed a new set of protocols for conducting toxicity tests, focused on providing consistent detailed analytical chemistry, environmentally realistic exposure regimes, and standard methods for solution preparation. These protocols offer a baseline set of standard procedures which may be used by other laboratories to develop comparable data sets. Overall, the following conclusions are proposed by the CROSERF:

The research and regulatory community benefit from the judicious use of standardized protocols. Proposed modifications must be weighed against the loss of comparability.

- New data sets developed using new protocols need to be integrated into the existing data set; however, there is no organization which currently fulfills such a role.
- The applicability of the data obtained by using standard national test species is often a regional concern. The data here suggest that the results for the standard test species were not all that



different than the results for the regional species selected.

- Exposures to declining concentrations of dispersant alone, oil, or dispersed oil are less toxic than a constant exposure. It is believed that for most species the more rapid the dilution the greater the difference. This was tested with one dilution regime over 12 species, 7 oils and 2 dispersants. This relationship appears to be clear for all of the tested species except *M. beryllina*, which seems to be more sensitive to initial concentration, than it is to duration of exposure, suggesting a different mode of action for this species. Overall, however, the data support the conclusion that constant exposure testing does not realistically assess the risk to marine or coastal organisms where rapid dilution is possible.
- The dispersants tested (Corexit 9500 and 9527) appear generally less toxic than oil.
- There were large differences in toxicity between the various oils tested. It may be more important to vary the oils used than the species tested when assessing regional risks to oil spills.
- The toxic mode of action of water accommodated fractions and chemically enhanced-water accommodated fractions is potentially very different, due to the presence of bulk oil droplets in the latter, while the former is based on solubility.
- There appears to be no difference in the range of  $LC_{50}$ s between constant exposures to dispersed oil or water accommodated fractions. With spiked exposures, the same pattern was observed, indicating that dispersed oil is no more toxic than the water accommodated fraction of un-dispersed oil at equivalent exposures.
- Differences between the toxicity of water accommodated fractions created using weathered and fresh oil are inconsistent. Weathered oil (WAF) does not appear to be significantly less toxic, for either spiked or constant exposure. In the case of dispersed oil (CE-WAF), constant exposure values for fresh and weathered oil appear similar, but for spiked exposure, dispersed fresh oil was consistently more toxic than dispersed weathered oil. However, the differences were probably not large enough to make the risk from dispersing fresh oil appreciably greater, provided that rapid dilution is possible.
- The range of average  $LC_{50}$  values for spiked exposure to fresh dispersed oil was 2.3 to 48.6 ppm. This suggests that as long as dilution was occurring at least as rapidly as the 2.5 hour half-life used in the CROSERF protocols, a threshold of 1 ppm would probably represent a reasonable level of protection for more sensitive life history stages of animals in the water column.
- It is reasonable to ask if  $LC_{50}$  values are the appropriate measure to use to set thresholds. It might be beneficial to examine the use of “lowest observed effects level” or other value instead. This is, however, not a simple determination, given that almost all of the extant data reports  $LC_{50}$  values.

Aurand, D., and G. Coehlo, “Net Environmental Benefit (Ecological Risk) Assessment: Consensus Workshop. Environmental Tradeoffs Associated With Oil Spill Response Technologies. Upper Mississippi River” Ecosystem Management & Associates, Inc. Lusby, MD., Technical Report 04-02, <http://www.ecosystem-management.net/c/7/project-reports>, 48 p., 2004.

In March and April 2004, the United States Coast Guard and the US Environmental Protection Agency (US EPA) sponsored two workshops in separate locations along the upper Mississippi River to evaluate the relative risk to natural resources from various oil spill response options. The first examined a Canola oil spill from a railroad accident into Pool 7 of the Mississippi River. The second, held in Keokuk, Iowa, examined a pipeline rupture that released

West Texas Intermediate crude oil into Pool 19. Both exercises were assumed to occur in the fall, and so the primary concern was for protection of migrating waterfowl. In both exercises, there were also concerns about effects on protected species of mussels. In both areas the spill affected most of the pool within the first 24 hours, so many of the impacts were judged to be unavoidable. Shoreline cleaning and nearshore recovery of pooled oil was judged effective in both areas in preventing reoiling, but participants were concerned about additional damage to sensitive habitats in both workshops. In Pool 19, participants felt that an early deployment of deflection booming offered the best option to protect waterfowl. In both areas, the ecological damage to migrating populations of waterfowl could be serious if the response options were not rapidly applied and effective, since very large populations of birds, in some cases the majority of the continental population, use the pools during migration.

Aurand, D., M. Hitchings, L. Walko, J. Clark, J. Bonner, C. Page, R. Jamail and R. Martin, *Texas General Land Office 'Spill of Opportunity' Dispersant Demonstration Project Description*, Report 01-08A, Ecosystem Management and Associates, Inc., Lusby, Maryland, 156 p., 2004.

The background information and operational design is given for a field program to evaluate dispersant use in an estuary. The highest probabilities were given as in Galveston Bay and Corpus Christi Bay. The potential environmental risks and benefits associated with the application of dispersant to oil spills up to 500 barrels were evaluated. It was concluded that the risk is low especially for up to 250 barrel oil spills. A plan was developed which including aircraft for application and spotting. A surface boat crew would collect fluorometry data in the water column as well as water samples, sediment samples and shellfish tissue samples. The analysis of these samples should then provide analysis of the effectiveness of the application and an estimate of the effects of the application on the fauna of the area.

Barron, M.C., M.G. Carls, J.W. Short and S.D. Rice, *Photoenhanced Toxicity of Aqueous Phase and Chemically-Dispersed Weathered Alaska North Slope Crude Oil to Pacific Herring Eggs and Larvae*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 30 p., February, 2002.

Most of the available data on the toxicity and risks of oil and chemically-dispersed oil have been derived from laboratory studies that do not incorporate exposures to the ultraviolet radiation (UV) that occurs in aquatic environments. UV contains light energy that can be absorbed by specific components in oil, including PAHs (polycyclic aromatic hydrocarbons). The UV that is present in aquatic environments includes UVB (280 to 320 nm) and UVA (320 to 400 nm). Understanding photoenhanced toxicity is important because petroleum and weathered oil is known to be phototoxic, exhibiting a two to greater than 1000 fold increase in toxicity in the presence of UV compared to standard laboratory lighting conditions with minimal UV. The photoenhanced toxicity of Alaska North slope crude (ANS) to Alaskan fish species has never been determined, and the potential for photoenhanced toxicity of chemically-dispersed ANS has not been previously evaluated in any species.

This study investigated the photoenhanced toxicity of weathered ANS to eggs and larvae of the Pacific herring (*Clupea pallasii*), and the relative toxicity of chemically-dispersed and aqueous phase oil. Aqueous phase oil is the portion of petroleum that dissolved or accommodated into the water used in toxicity tests. Herring are known to be sensitive to ANS at concentrations as low as 0.4 µg/L (parts per billion) of total PAHs (tPAH; sum of all individual PAHs that were quantified). Herring were exposed to a series of aqueous phase doses prepared with high energy

mixing of ANS with the chemical dispersant Corexit 9527 either present or absent. Herring eggs (a few days after fertilization) and larvae (a few days after hatching) were exposed to a combination of oil, dispersant, and UV treatments in the laboratory, with some UV exposures occurring outdoors in sunlight.

Oil exposures occurred at only one life stage of herring, either in embryos or larvae. Following oil exposure, each life stage was exposed to UV treatments: control lighting or UVA (eggs and larvae), or sunlight treatments (only larvae). UV treatments with significant UVB (sunlight, UVA+sunlight) were only performed in the larval experiments because the potential importance of UVB in the photoenhanced toxicity of ANS to herring was not recognized until egg exposures were completed. A separate larval experiment was conducted to discriminate between two possible modes of action of the photoenhanced toxicity of oil, photosensitization (activation of hydrocarbons that have bioaccumulated in tissue) or photomodification (photooxidation of hydrocarbons in water). Based on prior studies with oil and components of oil, the group hypothesized that weathered ANS would have a photosensitization mode of action (phototoxicity after fish first accumulate oil residues).

Barron, M.C., *Critical Evaluation of CROSERF Test Methods for Oil Dispersant Toxicity Testing under Subarctic Conditions*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 18 p., January, 2003.

This review critically evaluates the aquatic organism toxicity testing protocols developed by the Chemical Response to Oil Spills: Ecological Research Forum (CROSERF) for applicability to assessing chemical dispersant toxicity under subarctic conditions. CROSERF was established as a working group of industry, government, and university scientists to coordinate and disseminate research on chemical oil spill dispersants. CROSERF participants developed aquatic toxicity testing protocols during 1994 to 2000 with the foremost objective of standardizing test methods and reducing inter-laboratory variability. A number of refinements are recommended to adapt the CROSERF protocols for testing with subarctic species under conditions of expected longer oil persistence. Recommendations were focused on providing toxicity test data most relevant to risk management decisions regarding dispersant use in subarctic environments, rather than the primary CROSERF objective of standardizing procedures. Recommended refinements of the CROSERF protocols include (1) testing both a fresh and moderately weathered oil under conditions of moderate mixing energy, (2) testing both Corexit 9500 and 9527 using a high dispersant:oil ratio, (3) preparing toxicity test solutions using variable dilutions rather than variable loading, (4) using static exposures in open chambers, (5) increasing the duration of tests from 4 days to 7 days to allow assessment of delayed mortality, (6) quantifying approximately 40 polycyclic aromatic hydrocarbons (PAHs) and their alkyl homologs (predominant petroleum PAHs) in the toxicity test solutions, (7) testing Pacific herring larvae, an urchin species, and a calanoid copepod under subarctic conditions of temperature and salinity, (8) assessing the potential for photoenhanced toxicity by incorporating a limited exposure to sunlight or simulated natural sunlight, and (9) incorporating a bioaccumulation endpoint by measuring PAH accumulation in copepod tissue. Refinements in the preparation of oil dosing solutions, exposure and light regimes, and analytical chemistry should increase the utility of the test results for interpreting the toxicity of chemically dispersed oil and making risk management decisions regarding dispersant use under subarctic conditions.



Belore, R., "The history of Chemical Dispersants in the United States", In *Oil Spill Symposium 2004: New Dimension in Oil Spill Response after the Prestige: Compensation and Response Technology*, Tokyo: Petroleum Association of Japan. 8 p., 2004.

A review of the history of dispersant workshops given by S.L. Ross Environmental research is given. Focus is primarily on the workshops given in the USA. The message of these workshops is to dispel fears related to dispersant use.

Belore, R., "Identification of Window of Opportunity for Chemical Dispersants on Gulf of Mexico Crude Oils", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 29 p., 2007.

The objective of this study was to develop best-fit correlations between readily available fresh oil properties and the window of opportunity for successful chemical dispersant use using data from Gulf of Mexico (GOM) crude oils. Detailed fresh and weathered oil property information was acquired from Environment Canada's oil property database and processed to derive the oil parameters required by the SL Ross Oil Spill Model (SLROSM) to complete detailed oil spill behavior modeling for each oil as a function of spill type and environmental conditions. The results from the spill modeling were used to identify the time window for successful chemical dispersion of 1,000 and 10,000 barrel batch spills using average environmental conditions. The time that the model predicts that the oil's (or emulsion's) viscosity reaches 7,500 cP has been used as the maximum time-window for chemical dispersant use. Dispersant has also been deemed ineffective if the oil's pour point exceeds the ambient water temperature by 15°C. This criterion was applicable for only one of the oils studied (Mississippi Canyon Block 194). The time windows identified using the spill behavior modeling have been correlated with the following independent fresh oil properties: API gravity, flash point, pour point, viscosity, boiling point distribution, wax content, asphaltene content, resin content, sulfur content, aromatic content and saturate content.

Various single- and multiple- parameter correlations were completed to identify the best-fit correlations between the commonly available fresh oil properties and the modeled time window for successful dispersant use. The combination of sulfur, saturate and wax contents of the fresh oils correlated best with the time window for dispersant use for both the 1,000 and 10,000 barrel spill scenarios. The best model identified for the 1,000 barrel spill is: Dispersant Time Window (hr) =  $\exp(-1.997657 \cdot \text{Sulfur} + 0.107833 \cdot \text{Saturate} - 0.326005 \cdot \text{Wax} - 1.35108)$  (all input fresh oil property data in wt %)

The best model identified for the 10,000 barrel spill is: Dispersant Time Window (hr) =  $\exp(-1.30926 \cdot \text{Sulfur} + 0.05534 \cdot \text{Saturate} - 0.28146 \cdot \text{Wax} + 2.7153)$

Bordbar, L., S. Oryan, M. Emtiyazjoo, and D. Farkhani, "The Effect and the Toxicity of Iranian Oil Dispersant (Pars I) on Rainbow Trout", Paper presented at the *WIT Transactions on Ecology and the Environment*, Vol. 88, pp. 79-88, 2006.

Toxicity and effectiveness testing were carried out on a new dispersant, PARs I. The 96-hour LC50 to rainbow trout was 17 mg/L compared to 490 mg/L with an oil dispersant mix. The effectiveness was compared to another product without details of testing method.

Brady, B.A., *Oil Spill Dispersants and Temperate Marine Environments: A Literature Review to Support Development of Dispersant Use Protocols for Victoria*, Report to Marine Safety Victoria, Queenscliff, Vic., Marine and Freshwater Resources Institute., 86 p., 2002.

This review is to provide background information to support development of dispersant use protocols for Victoria, Australia. Dispersants are recognized as one of several possible oil spill

response options and has the advantage of potentially removing a greater proportion of oil from the water surface than physical methods, thereby preventing it from reaching the shore and affecting wildlife. However, if used inappropriately, dispersant use can result in environmental harm. Different resources are at varying risk of exposure to untreated oil and chemically dispersed oil during a marine oil spill incident. Dispersants will potentially increase the exposure to chemically dispersed oil for water column and bottom dwelling resources, while reducing exposure for surface dwelling and intertidal resources. Thus there needs to be a trade-off between effects of dispersed oil in the water column versus effects of untreated oil on the shoreline and intertidal zone in the form of a net environmental benefit analysis during dispersant decision making.

Cedre, F. Merlin, Editor, *Using Dispersants to Treat Oil Slicks at Sea: Airborne and Shipborne Treatment Response Manual*, [www.cedre.fr/](http://www.cedre.fr/), 56 p., 2005.

This is a manual on both airborne and shipborne application of oil spill dispersants.

Cooper, D., K. Volchek and W. Wong, "Process for the Removal of Spent Oil Spill Dispersants From Test Water at the National Oil Spill Response Test Facility", SAIC for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 46 p., 2003.

Testing was carried out to see if membrane technology could be used to remove surfactants from water after dispersant experiments. It was found that the G50 membrane had poorest dispersant and oil rejection although it had highest permeate flux. The NF45, Desal 5, G10, and G20 had very good rejection, with the G20 having the highest flux rate of the four. Because of these facts, the G20 was selected as the recommended membrane for the OHMSETT application. The results of the membrane testing indicate that it is possible to separate surfactants from water using membrane technology. Problems with relatively low flux rates, however, indicate that a relatively large membrane system would be required to clean the OHMSETT tank. A preliminary cost estimate was obtained for a system with the following parameters: Membrane: G20 (Osmonics, Inc.; MWCO: 3500 Daltons), permeate flux of 20L/m<sup>2</sup>/hr, with a volume recovery of 90%. Pilot scale testing would be strongly recommended in order to provide cost estimates due to scaling factors.

CRC, Coastal Response Research Center, *Research and Development Needs for Making Decisions Regarding Dispersing Oil*, University of New Hampshire, Durham, N.H., [http://www.crrc.unh.edu/dwg/dispersant\\_workshop\\_report\\_complete.pdf](http://www.crrc.unh.edu/dwg/dispersant_workshop_report_complete.pdf), 29p., 2006.

This reports on a workshop to discuss dispersant research priorities. There were common action items identified across the groups:

- Expansion of data-mining and literature syntheses for efficacy and effects
- Improvement in designing studies and analytical protocols to allow better inter-comparisons among studies
- A return to bench-scale testing to fill basic gaps that still exist
- Better field monitoring methods and technologies at spills-of-opportunities
- Development of integrated models to assist decision makers on dispersant use during planning and emergency response.

Crescenzi, F., M. Buffagni, E.D. D'Angeli and F. Porcelli, "A New Biosurfactant for Use in the Clean Up of Oil Spills on Sea Water Environment", in *Proceedings of the First International Conference on Oil and Hydrocarbon Spills, Modelling, Analysis and Control: Oil Spill III*, Ed. C.A. Brebbia, WIT Press, Southampton, United Kingdom,

pp. 245-251, 2002.

A biosurfactant composed of a polymeric polysaccharide chain with linked fatty acid chains of 10 to 14 carbon chains in length. The biosurfactant behaves as dispersant and aids in ultimate oil breakdown. Small-scale testing was reported.

Davies, L., F. Daniel, R. Swannell and J. Braddock, "Biodegradability of Chemically-Dispersed Oil", AEA Technologies for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 49 p., 2001.

A number of microcosms were analyzed to examine oil biodegradation with and without dispersants. Oil degraders proliferated in all biologically-active microcosms. Maximum microbial growth rates for the dispersant tests were approximately one fifth of those observed with Forties at 15°C, presumably reflecting slower growth on oil at the lower temperature of 8°C. In the absence of the dispersant, the onset of colonization was delayed, although microbial growth rates and population sizes were greater than had been observed previously with Forties crude oil. This difference probably reflects the greater natural dispersion seen with ANS at 8°C, than was seen with Forties at 15°C. The utilization of hexadecane as a carbon source leading to the formation of carbon dioxide and water is called hexadecane mineralization. The hexadecane mineralization results suggest that n-alkanes biodegradation was occurring in the natural dispersion tests. They also suggest that in presence of dispersant the rate of mineralisation was increased. This observation is supported in part by the oil chemistry analysis, but less oil degradation was observed with ANS at 8°C than was found with Forties at 15°C. In conclusion, there is evidence that dispersant addition promotes the biodegradation of ANS crude oil at 8°C, but, the effect is much smaller than that observed with a more dispersible and biodegradable oil (Forties) at 15°C. From the results of the present work, it is not possible to conclude whether this is due to the different nature of the oil or to the effect of temperature or to a combination of both parameters. It was recommended to run a set of experiments with ANS crude oil at 15°C, or with Forties crude oil at 8°C to determine which of the parameters is reducing the effect of dispersant on the biodegradation of oil under simulated marine conditions.

DeCola, E., *Review of Oil Spill Responses on Moderately-Sized Spills in US Waters from 1993-2000*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrac.org/projects/EnvMonitor/dispers.html>, 9 p., March, 2004.

A review of nearshore oil spill responses on moderately sized oil spills (500 to 4,000 barrels) in the United States from 1993 to 2000. The review categorized responses by type: mechanical, dispersants, in situ burning, or a combination of the responses on any one spill. The best estimate of efficiency for each of the responses used on each specific spill was to be noted, but only few data were available. No dispersant use was documented in the OSIR data base used for this study.

DeCola, E., *Dispersant Use in Oil Spill Response: A Worldwide Legislative and Practical Update*, Aspen Law and Business, New York, 314 p., 2003.

This book reviews dispersant topics and use worldwide. Much of the coverage is similar to the predecessor book and covers the period from about 1990 and on to about 2000, with some coverage from 2000 to 2002.

Decola, E., and M. Fingas, *Observers' Report, MMS Cold Water Dispersant Tests, Ohmsett Testing Facility 28 February – 3 March 2006*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrac.org/projects/EnvMonitor/dispers.html>, 27 p., May, 2006.

The PWS RCAC observer team attended the OHMSETT dispersant tests to monitor several issues of concern, which were: (1) heating of oil; (2) artificial weathering of oil, (3) use of booms in testing field; (4) re-surfacing of oil; (5) tank contamination; (6) use of oils which are not typically transported; (7) herding using fire hoses; and (8) uncontrollable natural factors. The PWS RCAC observer team concluded that the test procedures adequately addressed concerns regarding heating of oil and use of booms in the testing field. The test oil matrix included both artificially weathered oil and oil that had been weathered on the tank; presumably, the investigators report will address the differences between the two methods. The PWS RCAC observer team noted significant resurfacing of oil following each dispersant test. Oil that resurfaces at the end of a test was not accounted for by the investigators, and no mass balance calculations were undertaken. The testing procedures continue to use fire hoses to herd remaining surface oil for collection; this was observed to have the unintended consequence of temporarily re-dispersing oil, especially for the dispersant tests. Tank contamination continued to be an issue, and sheening was visible throughout the test period as well as the prominent oil stain around the edges of the tank. PWS RCAC concerns regarding the test oils were not addressed in these trials. The Alaska crude oils tested were obtained directly from the production facilities on the North Slope, rather than in Valdez at the terminus of the Trans Alaska pipeline. Therefore, the test oils vary in composition from oil that might actually be spilled in Prince William Sound. Because the OHMSETT facility is open to the elements, the impact of uncontrollable natural forces continues to be a concern. In addition to these issues, the PWS RCAC noted several additional concerns regarding the experimental design and interpretation of results from these trials. These include: the inability to derive effectiveness values in the absence of mass balance calculations; the impact of residual dispersant and surfactant in the tank during the test period; the practice of spraying dispersants immediately after the oil is applied and before any appreciable slick can form; and the fact that the dispersant-to-oil ratio used in the tests was significantly higher than the 1:20 dosage recommended for use in U.S. waters.

Deshpande, N., S. Chandrasekar, G.A. Sorial and J.W. Weaver, "Dispersant Effectiveness on Oil Spills: Impact of Environmental Factors", ICES CM 2005/S: 30, in *Proceedings of the 2005 ICES Annual Science Conference*, International Council for the Exploration of the Sea, Copenhagen, Denmark, 10 p., 2005.

In this dispersant laboratory study, three salinity values in the range of 10-34 ppt (parts per thousand) were investigated. Three oils were chosen to represent light refined oil, light crude oil and medium crude oil. Each oil was tested at three weathering levels to represent maximum, medium and zero weathering. Two dispersants were chosen for evaluation. A modified trypsinizing flask termed the 'Baffled Flask' was used for conducting the experimental runs. A full factorial experiment was conducted for each oil to investigate the effect of salinity on three environmental factors: temperature (4 levels), oil weathering (3 levels) and mixing energy (150, 200 and 250 rpm). Each experiment was replicated four times in order to evaluate the accuracy of the test. Statistical analyses of the experimental data were performed separately for each of the three oils three times (with or without dispersant). A linear regression model representing the main factors (salinity, temperature, oil weathering and flask speed) and second order interactions among the factors were accurately fit to the experimental data. Salinity was found to play an important role in determining the significance of temperature and mixing energy on dispersant effectiveness for almost all the oil dispersant combinations.

EFRA, *Specification for Oil Spill Dispersants*, Department for Environment, Food and Rural Affairs, Great Britain., London, <http://www.defra.gov.uk/environment/water/marine/uk/oilspill/lr448.pdf>, 11p., 2007.

This is the official British government specification for oil spill dispersants. Three types are defined as:

Type 1: Conventional Hydrocarbon-base - for use primarily undiluted on beaches, but may also be used undiluted at sea from WSL spray sets using breaker boards or other suitable means of application and agitation.

Type 2: Water-dilutable concentrates - for use at sea after dilution 1:10 with seawater, and sprayed from WSL spray sets using breaker boards or other suitable means of application and agitation.

Type 3: Concentrate - for use undiluted from aircraft, ships or on beaches, using appropriate spray gear.

The Warren Springs test is defined as the efficacy test.

Fingas, M.F., *A Review of Literature Related to Oil Spill Dispersants Especially Relevant to Alaska*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, Alaska, 48 p., 2002.

This paper is a review of the literature on oil spill dispersants published from 1997 to January, 2002. This is the predecessor to this report. The results of the review indicate that dispersant effectiveness continues to be a major issue and is unresolved for Alaska North Slope (ANS) crude oil. Results of one recent dispersant effectiveness study for moderate-energy apparatus demonstrate dispersant effectiveness values ranging from 5 to 15% for ANS crude oil. This study was conducted at water salinities and temperatures known to occur in Alaskan waters, specifically Prince William Sound. High-energy tests such as the MNS, IFP, and EXDET demonstrate higher dispersant effectiveness results, however, the temperatures and salinities used are outside the range of those known for Prince William Sound. New studies question the high values of such tests. Large-scale testing and field tests show effectiveness values that are fractions even of the moderate-energy tests. Since 1997, there have been numerous studies on the toxicity of oil and dispersed oil. Many of these indicated that the acute toxicity of chemically dispersed oil and physically (naturally) dispersed oil is different for different marine test species. In most of the cases, the chemically dispersed oil is somewhat more toxic than the physically dispersed oil. Studies of the food chain indicate that dispersed oil is more likely to result in the passing of naphthalene through the food chain. Similarly, body burdens of PAHs vary depending on the marine species and whether the oil is naturally or chemically dispersed. There is little new in operational matters regarding application of dispersants. The finding that Corexit 9500 is much less effective on thick oil slicks when applied diluted with water than when applied neat is, however, significant. A review of legislation shows that there are no significant changes in dispersant use policy in North America or Europe. There are only eight documented cases of dispersant use in the literature during this time period. One of these is in Nigerian waters, one in Australia, one in Israel, one in Venezuela, one in Britain, and the other three are in the U.S.

Fingas, M., *Weather Windows for Oil Spill Countermeasures*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 89 p., January, 2004.

A literature review was carried out to determine if there were data related to the performance of all countermeasures techniques under varying weather conditions. The literature did not show any quantitative guides for the performance of countermeasures under varying weather

conditions, however, data could be extracted from these to provide assessment of performance changes with weather conditions. The most important factors influencing countermeasures are the wind and wave height. These two factors are related and given a typical sea can be inter-converted, however these must sometimes be considered separately so that specific weather effects can be examined. Other weather conditions include currents and temperature. Currents are important in that they become the critical factor for countermeasures such as booms. Temperature effects are primarily relevant to dispersants and have been shown to have minimal effect on other countermeasures.

The weather effects on dispersant application and effectiveness is threefold: the amount of dispersant that contacts the target is highly wind dependent, the amount dispersed on the surface is very dependent on ocean turbulence and other energy, and the amount remaining in the water column is dependent on the same energy. Nomograms for effectiveness have been created. At high sea energies, many lighter oils can disperse naturally.

The weather effects on other countermeasures methods have been summarized.

Fingas, M.F., *A Guide to Chemical Dispersion*, Senes Consulting for the South American Petroleum Association, Ottawa, Ontario, 30 p., 2005.

This document provides guidance on decision-making for dispersion of oil spills. It contains a compilation of information about chemical dispersion of oil spills and includes the scientific aspects of the dispersion process and its effects, examples from the extensive testing and use of chemical dispersants, and practical information about the procedures to be followed and equipment required for carrying out such a dispersion operation.

Fingas, M., *A Survey of Tank Facilities for Testing Oil Spill Dispersants*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 59 p., May, 2005.

This report is a survey of tank facilities that could be used for testing oil spill dispersants. The report begins with considerations for tank testing, followed by a list of requirements for tank testing, and data is then provided on a number of potential tanks. Issues related to conducting dispersant tests in large tanks that are to be used for testing dispersants include: ability to filter or renew tank water; ability to use the tank to conduct experiments; ability to apply dispersants and take measurements; availability of wave-making apparatus; ability to calculate mass balance; ability to control or manipulate water temperature; and ability to run tests under different salinities. In compiling this report, a survey of tanks was carried out. Most of the information came from the Internet or by contacting individuals. The tanks that were found to meet most of the criteria are the Texas A&M SERF tank at Corpus Christi and, to a lesser degree, the new EPA/BIO tank at Dartmouth, Nova Scotia. Special features of the SERF tank include nine parallel tanks so that experiments can be carried out simultaneously, extensive water treatment facilities, an adjoining laboratory, and high-precision wave-generators. Disadvantages include the narrowness of the tanks, the lack of built-in water temperature controls, and the location in the south, although a design for a climate-controlled facility has been completed. SERF is the only facility that would be ready to go for dispersant testing according to the requirements noted in this report. The new EPA/BIO tank at Dartmouth will also be of interest to the Prince William Sound Regional Citizens' Advisory Council as it is built especially for testing dispersants. The advantages of this facility include its location close to the sea. Disadvantages are that it is new



and calibration, testing, and establishment of basic parameters will have to be completed before the facility is ready for use. Sixty tanks are listed in this report. The most significant ones are listed and summarized and the tanks of particular interest are noted.

Fingas, M.F. and E. DeCola, *Oil Spill Dispersant Effectiveness Testing in OHMSETT*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska,

<http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 27 p., May, 2006.

This paper is a review of some recent dispersant testing at OHMSETT. Ten dispersant tests were observed, 5 dispersant tests and 5 control tests with Alaskan oils. The dispersant tests showed good initial dispersion and subsequent observation showed much of the oil from these tests re-surfaced, about half within about one to two hours and most of it by next morning. The testing method was viewed with respect to concerns raised earlier from observing and analyzing other tests. First, a report sponsored by PWS RCAC, had raised 17 concerns about dispersant tank testing. These were 17 critical factors, identified in an earlier study, that need to be considered and included in any test for measuring the effectiveness of dispersants in a tank in order for that test to achieve useful results. The National Academy of Sciences reviewed dispersant testing and noted the following concerns:

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

In addition, there were several concerns raised by PWS RCAC:

1. heating of the oil, 2. artificial weathering of the oil, 3. use of booms in testing field, 4. re-surfacing of the oil, 5. tank contamination, 6. use of oils which are not typically transported, 7. herding, and 8. uncontrollable natural factors.

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

1. The experiment is ended at the peak of dispersion and before re-coalescence occurs. Extensive re-surfacing of the oil can readily be seen after the experiment is terminated and within 1 hour of the start of the experiment.
2. No mass balance is attempted and data collected are not used to attempt mass balance.
3. Some oil was collected to presumably determine amount dispersed, however this was always

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

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

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

Fingas, M., *Dispersants, Salinity and Prince William Sound*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, 48 p., <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, December, 2004.

This paper is a summary of the effects of water salinity on chemical dispersion, especially those effects related to effectiveness. A surfactant, the operative dispersant ingredient is more lipophilic, or oil-loving, in freshwater and increases in hydrophilicity (or water-loving) as the salinity rises. The stability of the resulting droplets is also dependent on salinity. This is due to the increasing ionic strength of the water as salinity rises. As the salinity rises above a certain point, which depends on the particular type of surfactant, this increased force results in more surfactant molecules leaving the oil drop entirely. While the theoretical possibility of freshwater dispersants exist, the stability of dispersions in less saline waters would be less. There is a body of literature on the use of surfactants for secondary oil recovery. There are some commonalities among the many findings. Recovery efficiency falls off at both high and low salinities. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant. The consensus of several papers is that the solubility of the hydrocarbon increases with increasing salinity and is low at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25 to 35 o/oo. A number of physical systems involving surfactants and salinity changes are reported in the literature. Included in these is the finding that the stability of microemulsions is greater at salinities of 25 to 35o/oo. Some workers found that the stability of systems was very low in fresh water or in water with salinities of < 10 o/oo.

Some field studies of dispersant application were conducted in the freshwater environment. While effectiveness was not specifically measured, it was noted in both series of studies that effectiveness may have been low. In the one study, the investigators noted that the surfactants had poor effectiveness and stability in freshwater. In this particular case, the dispersion lasted only for about an hour and the dispersion was limited to a few centimetres. In another case, it was noted that there was oil around the edges of the dispersed pond within a short time of dispersant application.

The varying salinities of the waters in Prince William Sound were described and summarized. There are areas around the Sound of low salinity. Dispersant applications in these areas would result in reduced dispersant effectiveness.

The following are the overall conclusions of this study.

a) The effectiveness of conventional and currently available dispersants is very low at 0 o/oo or sometimes they are completely ineffective. b) Dispersant effectiveness peaks at 20 to 40 o/oo. This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity



but still shows a peak at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and with others at about 35 o/oo. c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and as it exceeds this value. d) While there is some evidence for a temperature-salinity interaction, as noted in the data of Moles et al., 2002, there are not enough data to make solid conclusions. e) Recent data are largely taken using Corexit 9527 and Corexit 9500. Since these have the same surfactant packages, there is a concern that the results may be more relevant to these formulations than to others. f) Observations on two field trials in freshwater appear to indicate that the laboratory tests are correct in concluding very low freshwater effectiveness. g) There were few studies on the biological effects of oil with varying salinity. h) The findings in the dispersant literature summarized in this study are in agreement with the theoretical and basic surfactant literature. i) The salinity of the waters in Prince William Sound is typically high in the centre of the Sound, but is sometimes low, especially near river outfalls, and in fjords with tidewater glaciers. The salinities in these areas, often less than 15 o/oo, will result in lower dispersant effectiveness.

Fingas, M., *A White Paper on Oil Dispersant Testing in Large Tanks*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 26 p., November, 2002.

A perspective on testing the effectiveness of oil spill dispersants in large tanks is given. Literature that relates to testing methodology is reviewed. The following are 17 critical factors that need to be considered and included in any test for measuring the effectiveness of dispersants in a tank in order for that test to be valid. These factors are reviewed in this assessment.

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

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

Fingas, M., *A White Paper on Oil Dispersant Field Testing*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 27 p., May, 2002.

This white paper is a perspective on the field testing of the effectiveness of oil spill dispersants. All field tests conducted to date are briefly reviewed and literature that relates to testing methodology. Twenty-five considerations on the field testing of dispersants were discussed:

- |                      |  |
|----------------------|--|
| 1. Mass balance      | 14. Visibility of oil from the surface |
| 2. Proper controls   | 15. Background levels of hydrocarbons  |
| 3. Analytical method | 16. Fluorescence of dispersant         |

- |   |  |
|---|--|
| 4. Differential plume movement                  | 17. Herding                                |
| 5. Time lag and length of time followed         | 18. Emulsion breaking                      |
| 6. Mathematics of calculation and integration   | 19. Application success                    |
| 7. Lower and upper limits of analytical methods | 20. Heterogeneity of slick and plume       |
| 8. Use of remote sensing                        | 21. Deposition measurements                |
| 9. Thickness measurement                        | 22. True analytical standards              |
| 10. Behaviour of oil with surfactant content    | 23. Effect of wind on dispersant and slick |
| 11. Surfactant stripping                        | 24. Dispersant run-off                     |
| 12. Tracking surface oil and dispersed oil      | 25. Weathering of the Oil                  |
| 13. Recovering surface oil                      |  |

Each of these factors are noted as important to the appropriate outcome of the dispersant field experiment. The most important factors are the ability to determine a mass balance, use proper controls, analytical methods and to avoid procedures that will result in incorrect results.

Experimental design is discussed throughout this paper. Two experimental designs that are noted as very poor and would result in very large errors are described. The first one, the measurement of surface oil remaining after dispersant application on oil contained in the boom given that the currents/waves are near the critical loss velocity. Equations are shown that the loss of oil is strongly affected by the surface tension and the dispersant experiment as described is largely measuring containment loss and not dispersant effectiveness. The second experiment that results in very large errors is the integration of dispersed oil under the slick. The dispersed oil plume and slick do not have the same geometries and most often different trajectories. Integration under the slick over-estimates the dispersion by as much as a factor of 10.

Two experiments that could yield useful results are summarized. The first is a steady-state discharge of oil and dispersant in a constant current. The plume can be measured by in-situ fluorometry and integration. Since there is a steady state, this measurement can be taken at several points along the plume to confirm the effectiveness. The second one is an experiment where the concentration of oil in the water column after about 24 hours is used to define effectiveness. This method can only be applied in confined areas such as a test tank.

This report points out the technology and understanding that is necessary to conduct an accurate dispersant field test. There are many nuances, however these revolve around good chemistry, physics and understanding of the processes involved.

Fingas, M., "Review of Monitoring Protocols for Dispersant Effectiveness", Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska,  
<http://www.pwsrca.org/projects/EnvMonitor/dispers.html>, 88 p., August, 2003.

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 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 | 11. Controls               |
| 2. Safety                          | 12. Hydrocarbon background |

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
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.

Fingas, M., Z. Wang, B. Fieldhouse and P. Smith, *Chemical Characteristics of an Oil and the Relationship to Dispersant Effectiveness*, EE-173, Environment Canada, Ottawa, Ontario, 85 p., 2003.

Dispersant effectiveness data on 15 oils and their chemical and physical properties were measured. Additional data existed to make a total of 295 data points, although extensive compositional data existed only for the 15 oils. A total of 29 properties were correlated with the dispersibility of Corexit 9500 in the swirling flask apparatus. The highest correlation parameters were achieved with the content of nC12, naphthalenes, inversely with C26, the PAHs, and the sum of C12 to C18 hydrocarbons. This is highly indicative that the smaller aliphatic hydrocarbons up to C18 and the PAHs are the most dispersible components of oil. Furthermore, aliphatic hydrocarbons greater than C20 correlate inversely with the dispersant effectiveness, indicating that these hydrocarbons suppress dispersion. The correlations provide a unique insight into dispersant effectiveness. Thirteen models were constructed to predict the chemical dispersibility of oils. The simplest and best model is:  $\text{Corexit 9500 dispersibility (\%)} = -11.1 - 3.19(\ln \text{C12 content}) + 0.00361(\text{naphthalene content in ppm}) - 7.62(\text{PAH content squared}) + 0.115(\text{C12 to C18 content squared}) + 0.785(\% \text{fraction oil boiling below } 250^{\circ}\text{C})$ .

Models ranged from simple predictors involving only two parameters such as viscosity and density to 14-parameter models. The models developed were analysed statistically and the effectiveness was calculated for several dispersants. The more sophisticated models are able to predict dispersant effectiveness with high accuracy.

Fingas, M., *Stability and Resurfacing of Dispersed Oil*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 102 p., November, 2005.

This paper reviews the stability of chemically-dispersed oil which is known to destabilize after the initial dispersion. This is well documented in the surfactant and interfacial chemistry literature this is well known and there exists an extensive body of literature on this topic. Literature includes an abundance of experimental data on the topic as well as a great deal of theoretical approaches to the topic. This report will summarize both approaches. The phenomenon of oil resurfacing is the result of two separate processes: destabilization of an oil-in-water emulsion and the desorption of surfactant from the oil-water interface which leads to further destabilization. The de-stabilization of oil-in-water emulsions such as chemical oil dispersions is a consequence of the fact that all emulsions are not thermodynamically stable. Natural forces thus move the emulsions to an ultimate stable state, which are separated oil and water. What is important is the rate at which this occurs. An emulsion which stays sufficiently stable until long past its practical use consideration may be said to be kinetically stable. Kinetic stability is a consideration when describing an emulsion. An emulsion is said to be kinetically stable when significant separation (usually considered to be half or 50% of the dispersed phase) occurs outside of the usable time. There are several forces and processes which result in the de-stabilization and re-surfacing of oil-in-water emulsions such as chemically-dispersed oils. These forces include: gravitational forces, surfactant interchange with water and subsequent loss of surfactant to the water column, coalescence, flocculation, Ostwald ripening, sedimentation and creaming.

The most important force in re-surfacing of oil droplets from an oil-in-water emulsion is gravitational separation. Droplets in an emulsion will tend to move upwards when they have a density lower than that of water, this is true for all crude and petroleum dispersions that have a droplet with a density lower than that of the surrounding water. More dense oils, which would sink as emulsions, are poorly, if at all, dispersible. The rate at which oil droplets will rise due to gravitational forces is dependent on the density difference between the oil droplet and the water, the size of the droplets (Stokes' Law), and the rheology of the continuous phase. Further the rise rate is also influenced by the hydrodynamical and colloidal interactions between droplets, the physical state of the droplets, the rheology of the dispersed phase, the electrical charge on the droplets and the nature of the interfacial membrane. For crude oil-in-water emulsions such as dispersions, gravitational separation is the most important de-stabilization mechanism. Creaming is this de-stabilization process that is simply described by the appearance of the starting dispersed phase at the surface, without the processes in the intervening spaces being described. Creaming is the process that might be described in the oil spill world as re-surfacing.

Coalescence is an important de-stabilization process. Two droplets that interact as a result of close proximity or collision, can form a new larger droplet. The end results of these processes is to increase the droplet size, thus the rise rate and results in an accelerating destabilization of the emulsion. Coalescence has been studied extensively in oil-in-water emulsions. Studies show that Coalescence increases with increasing turbidity as collisions between particles are increased significantly.

Ostwald ripening is another process in the de-stabilization of oil-in-water emulsions. Ostwald ripening is the growth of larger emulsion droplets by absorption of soluble components or very small droplets from the water column. The effect is to remove soluble material from the water column, and smaller droplets, resulting in an increased growth of the larger droplets. The

phenomenon occurs because the soluble components of the disperse phase are more soluble in the larger droplets, than in the water and than in the smaller droplets. Although the Ostwald ripening phenomenon has not been investigated with oil-in-water emulsions to the same extent as other phenomena, it is believed to be important.

An important phenomenon in the consideration of dispersed oil stability is the absorption/desorption of surfactant from the oil/water interface. This process is stated to be the most important process for chemical process of surfactants and interfacial chemistry. When surfactants are dissolved in a bulk phase such as water, they start to be absorbed at the oil surface or interface. The system moves toward equilibrium, that is equilibrium amounts of surfactant at the interface and in the bulk phase. Desorption occurs primarily as a consequence of the lower concentration of surfactants in the bulk phase or water. The surfactants will transfer back and forth from the oil/water interface until an equilibrium of concentration in the interface or in the bulk liquid (water) is established. It is well known that in dilute solutions, that much of the surfactant in the dispersed droplets ultimately partitions to the water column and thus is lost to the dispersion process. Little, if any surfactant would partition back into the droplet in a dilute solution. This is the case for oil dispersions at sea. This is one important difference between dilute and concentrated solutions.

Examples of studies and models in all the processes are given as well as data from experiments and calculations. Data show that for a dilute solution such as a chemically-dispersed oil spill, half-lives would vary from 2 to 24 hours with a typical average value of 12 hours.

Gilson, D., "Report on the Non-Mechanical Response for the T/V Exxon Valdez Oil Spill", Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 14 p., August, 2006.

Within hours of the Exxon Valdez spill, the United States Coast Guard (USCG) discussed dispersant use with Alyeska and others. A trial run performed on the first day of the spill was determined to be ineffective. Massive herding was observed by the application crew. The effectiveness of two subsequent drops was inconclusive because of poor light and mechanical problems. The fourth drop had increased wave action that theoretically could have helped mix the dispersant. Increased winds hampered the fifth and sixth drops, and it was determined that the window for effectiveness had closed. The remaining four experimental applications in Blying Sound on April 2 and April 13 off Seward were ineffective due to the emulsification of the oil.

Guyomarch, J., E. Mamaca, M. Champs and F.-X. Merlin, "Oil Weathering and Dispersibility Studies: Laboratory, Flume, Mesocosms and Field Experiments", in *Proceedings of the Third Research and Development Forum on High-Density Oil Spill Response*, International Maritime Organization, London, United Kingdom, pp. 166-177, 2002.

Effectiveness tests on weathered oils were carried out in the Warren Springs and IFP tests as well as in the Polludrome. Effectiveness generally fell off exponentially in the tests, dropping to about 15% in the WSL test at 2000 mPa.s, to about 65% in the IFP test and about half way between in the mesocosm.

Kaku, V.J., M.C. Boufadel and A.D. Venosa, "Evaluation of Mixing Energy in the Swirling and Baffled Flasks", in *Oil and Hydrocarbon Spills III, Modelling, Analysis and Control* (Proceedings of the First International Conference on Oil and Hydrocarbon Spills, Modelling, Analysis and Control: Oil Spill III), Ed. C.A. Brebbia, WIT Press, Southampton, United Kingdom, pp. 211-218, 2002.

Two dispersant testing flasks, the swirling flask and the baffled flask, were evaluated for

energy using a hot-wire anemometer. It was found that in small portions near the center of the flask, that the average velocity in the baffled flask was five times the other unit. The velocity in the baffled flask was uniform with depth while this decreased significantly with depth in the swirling flask. The computed energy dissipation rates per unit length were about 0.03 in the swirling flask and about 0.92 in the baffled flask.

Khelifa, A., Fingas, M. and Brown, C.E., "Effects of Dispersants on Oil-SPM Aggregation and Fate in US Coastal Waters", Final Report submitted to the Coastal Response Research Center, University of Hampshire, NH, 53 p. and Annexes, 2008.

During marine oil spills, physically-dispersed oil droplets aggregate readily with suspended particulate matter (SPM) such as clay minerals or organic matters to form oil-SPM aggregates (OSAs). The simplest OSA consists of an oil droplet coated with micron-sized SPM. This project was a study of OSA formation in the laboratory using bench scale testing and natural sediments from five different US coastal waters. Parameters that were varied were oil type, sediment type and concentration, dispersant type and dispersant-to-oil ratio (DOR). The key objective of this research was to verify the above hypothesis stating that application of chemical dispersant in coastal water systems rich in SPM may enhance oil sedimentation due to OSA formation. Project results showed that OSAs do form readily with chemically dispersed oil and most of the natural sediments used in this project. Enhancement of oil sedimentation due to application of chemical dispersant was obtained in most of the experiments conducted in this study. The increase of oil sedimentation varied from insignificant to about 360%, compared to no chemical dispersant conditions. Fine content (the proportion of sediment grains less than 5.3 microns in size) in natural sediments, sediment concentration, oil viscosity, oil/brine interfacial tension and DOR are key factors that control the enhancement of oil sedimentation. Overall, the results showed that the more effective a chemical dispersant, the higher increase of oil sedimentation was measured. Also, significant enhancement of oil sedimentation was measured when concentration of SPM reaches a critical concentration equivalent to about 50% of oil concentration.

Koops, W., R.G. Jak and D.P.C. van der Veen, "Use of Dispersants in Oil Spill Response to Minimize Environmental Damage to Birds and Aquatic Organisms", in *Proceedings of the Third INTERSPILL Conference and Exhibition*, No. 429, [www.interspill.com](http://www.interspill.com), 21 p., 2004.

Literature on dispersant use is reviewed. The considerations for using dispersants are given. Potential benefits and harm are reviewed.

Koops, W., J.E. Tamis and R.H. Jongbloed, "Chemicals in Combating Oil Spills", in *Proceedings of the Third INTERSPILL Conference and Exhibition*, No. 442, [www.interspill.com](http://www.interspill.com), 21 p., 2004.

The use of treating agents generally is reviewed and the Netherlands approach to approving these is given.

Lewis, A., *Feasibility Study on the Use of Dispersants in the Bristol Channel in the Event of an Oil Pollution Incident: Final Report to English Nature and Countryside Council for Wales*, Wales: Cyngor Cefn Gwlad Cymru. 36p., 2002.

The use of oil spill dispersants in the Bristol Channel is considered. Factors in the Bristol Channel that need to be considered when deciding to use, or not to use, oil spill dispersants are described. Zones in the channel where dispersants can or cannot be used or alternatively, where special permission is required, are described.



Lewis, A., *Determination of the Limiting Oil Viscosity for Chemical Dispersion at Sea*, Maritime and Coastguard Agency, Southampton, U.K., [http://www.mcga.gov.uk/c4mca/research\\_report\\_516.pdf](http://www.mcga.gov.uk/c4mca/research_report_516.pdf), 87p. 2004.

Tests at sea were conducted to examine the limiting viscosity of oil for dispersion. At the conditions of testing were a sea temperature of 15°C, producing oil viscosities of 2,000 cP (IFO-180 grade fuel oil) and 7,000 cP (IFO-380 grade fuel oil) and waves associated with wind speeds of between 7 and 14 knots. The IFO-180 fuel oil appeared to be totally and rapidly dispersed by Dispersant C used at a nominal DOR of 1:25 at 12 knots wind speed. Dispersant B and Dispersant A appeared to be somewhat less effective, but still caused moderate dispersion when use at a nominal DOR of 1:25. At lower wind speeds of 7 to 8 knots, Dispersant C at a nominal DOR of 1:25 was seen to be less effective, but still appeared to cause moderately rapid dispersion of IFO-180. The IFO-380 fuel oil did not appear to be rapidly and totally dispersed by any of the three dispersants when used at any of the treatments rates, ranging from nominal DORs of 1:25 to 1:100 at wind speeds of 7 to 9 knots. At wind speeds of 13 - 14 knots, the performance of both Dispersant B and Dispersant C at a DOR of 1:25 improved to produce moderately rapid dispersion of IFO-380. The performance of Dispersant A was less than that of the other two dispersants, but was not tested at the highest wind speeds. The report concludes that some oil spill dispersants will be an effective response to oils with viscosity of 2,000 cP, but will not be effective on oils with a viscosity of 7,000 cP or more, in waves associated with wind speeds of 7 to 14 knots. The precise limiting viscosity between 2,000 and 7,000 cP is not known.

Lewis, A., F. Merlin, P. Daling and M. Reed, *Applicability of Oil Spill Dispersants Part I: Overview*, European Maritime Safety Agency (EMSA), Brussels, 91 p., 2006.

This is a summary of dispersants and their use to provide a manual for decision-support.

Lin, Q. and I.A. Mendelssohn, *Dispersant Effects on Fresh Marsh Vegetation: Toxicity Evaluation and Oil Remediation*, Louisiana OSRDP - Oil Spill Research and Development Program, Baton Rouge, LA., <http://www.osradp.lsu.edu/deliverables/2003/index.html>, 28 p., 2003.

Lin, Q. and I.A. Mendelssohn, *Dispersant Effects on Salt Marsh Vegetation: Toxicity Evaluation and Oil Remediation*, Louisiana OSRDP - Oil Spill Research and Development Program, Baton Rouge, LA., <http://www.osradp.lsu.edu/deliverables/2003/index.html>, 29 p., 2004.

The objectives of the proposed project were to evaluate the toxicity of dispersants on coastal fresh marsh plants by determining the dose-response of plants to dispersants, and evaluate the effect of different dispersed oils (crude oil and diesel fuel) on coastal fresh marsh plants by determining the dose-response of plants to dispersed oils. The dose-response of the fresh marsh plant *Sagittaria lancifolia* to the dispersant JD-2000 indicated that plant tolerance to this dispersant was relatively high. The marsh plant *S. lancifolia* was not impacted by the dispersant JD-2000 at dosages  $\leq 4,000$  ppm based on plant photosynthetic rate, plant mortality rate, and plant aboveground biomass. The results show that *Sagittaria lancifolia* can recover at dispersant dosages as high as 16,000 ppm, because the toxicity of the dispersant decreased during the 10 month experiment. In an experiment that determined the dose-response relationship and toxicity of dispersed oils to the fresh marsh plant *Sagittaria lancifolia*, plant photosynthetic rate, plant mortality rate, and plant aboveground biomass were negatively affected by the JD-2000 dispersed diesel at 16,200 ppm applied to the soil substrate. The  $LC_{50}$  (6 weeks) of dispersed diesel to *Sagittaria lancifolia* was estimated at 20,000 ppm. However, dispersed South Louisiana crude oil did not detrimentally affect *S. lancifolia* even at an oil dosage of 145,800 ppm. This indicated that

the toxicity of the dispersed oil primarily resulted from the oil itself, not from the dispersants. In an experiment that simulated oil dispersed before coming in contact with marshes, the dispersant JD-2000 greatly diminished the adverse effects of both diesel and crude oil. Without the dispersant, both diesel and crude oil significantly decreased photosynthetic rate and increased mortality even at a 50-ppm dosage. Two thousand ppm of diesel without the dispersant resulted in > 60% mortality of aboveground components. In contrast, neither the dispersed crude nor the dispersed diesel significantly affected *S. lancifolia* compared to the no-oil control. Application of the dispersant significantly reduced oil adsorption to the marsh sediment. Therefore, dispersant application greatly reduced oil impact on fresh marsh vegetation and sediment, indicating the potential of using dispersants as alternative countermeasures for oil spills in nearshore or estuarine environments.

LUMCON, *Dispersants Bibliography*, Louisiana OSRDP - Oil Spill Research and Development Program, Baton Rouge, LA., <http://www.osradp.lsu.edu/deliverables/2003/index.html>, 384 p., 2008.

This is a bibliography containing dispersant literature beginning at about 1990. Abstracts are also given.

Mearns, A., G. Watabayashi and J. Lankford, "Dispersing Oil Near Shore in the California Current Region", *California Cooperative Oceanic Fisheries Investigations Report (CalCOFI)*, Vol. 42, pp. 97-109, 2001.

A mathematical model was used to develop scenarios for evaluating nearshore alternative countermeasures on the California coast. A worst-case scenario was used and five options were compared, no response, mechanical response, burning and two levels of dispersants. During the first several hours following dispersal, the simulated dispersed oil concentrations exceeded guidelines for the early life stages of fishes and zooplankton. Adult fish and crustaceans were at risk for two hours. Dispersants would substantially reduce the amount of both floating and stranded oil relative to the other options. Higher levels of dispersants would remove more oil. These hypothetical risk assessments showed that chemical dispersion could reduce the impact of a nearshore oil spill.

Mitchelmore, C.L., J.E. Baker, "Acute and Chronic Effects of Oil, Dispersant and Dispersed Oil to Sensitive Symbiotic Cnidarian Species, Including Corals", University of New Hampshire, Coastal Response Research Center, Durham, N.H., [http://www.crrc.unh.edu/dwg/research/mitchelmore\\_progress\\_report\\_101705.pdf](http://www.crrc.unh.edu/dwg/research/mitchelmore_progress_report_101705.pdf), 8p., 2005.

This is an interim progress report on this study. A final report has not yet been posted.

Mochalova, O.S., N.M. Antonova, and L.M. Gurvich, "The Role of Dispersants in the Processes of Oil Transformation and Oxidation in Aquatic Environment", *Water Resources*, Vol. 29, 202-205, 2002.

This is a review of several options to treat oil spilled in Russia. It is suggested that some dispersants may help in the oxidation or biodegradation of oil, others not. As the paper has been translated from Russian, it is sometimes difficult to understand.

Moldestad, M.O., P.S. Daling and I. Singsaas, "Weathering and Chemical Dispersibility of Heavy Fuel Oils in Cold Waters", in *Proceedings of the Third Research and Development Forum on High-Density Oil Spill Response*, International Maritime Organization, London, United Kingdom, pp. 133-148, 2002.

This is a review of Norwegian studies on the dispersability of heavy fuel oils, primarily IFO-180. Tests were carried out at small scale and at larger scale in a meso-scale tank. Results were incorporated into a model. The findings are that the dispersability of IFO-180 varies with the source - ie. the refinery that it comes from. Some were easily dispersed, others not.



Mullin, J.V., "Dispersant Effectiveness Experiments Conducted on Alaskan and Canadian Crude Oils in Very Cold Water", in *Proceedings of the Third INTERSPILL Conference and Exhibition*, No. 468, [www.interspill.com](http://www.interspill.com), 19 p., 2004.

This paper is a review of the early testing of four Alaskan crude oils with Corexit 9527 and 9500, at the OHMSETT facility. The oils were weathered before application in the test. In the series of tests, effectiveness as high as 90% was claimed.

Nuka, "Non-mechanical Response Gap Estimate: Literature Review and Recommended Limits", Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 12 p., August, 2007.

This report recommends operational limits to dispersant and in-situ burning in terms of wind, sea state, air temperature, and visibility. These are based on literature testing and estimates.

Nuka, "Non-mechanical Response Gap Estimate for Two Operating Areas in Prince William Sound", Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, 36 p., April, 2008.

The "response gap" is the window between the upper limits of the response system (in terms of environmental conditions) and the conditions at which Hinchinbrook Entrance is closed to laden tankers. A methodology was developed to estimate the response gap by comparing response limits for dispersant and in-situ burning tactics to environmental conditions data from 2000-2005. A Response Gap Index was used to estimate how often a specific response tactic would be effective in a particular operating area. When one environmental factor would preclude a response completely, or two environmental factors would compromise a response, then a response is judged not possible for that time period. This study indicates that:

- Dispersant application in the Central Sound is not possible 75% of the time year-round, mostly because of darkness and conditions too calm for dispersant mixing.
  - Dispersant application at Hinchinbrook Entrance is not possible 80% of the time year-round, mostly because of darkness, conditions too rough for application, or too calm for mixing.
- These were compared with the results of the mechanical response gap estimate for the same two operating areas of Prince William Sound, concluding:
- When all technologies are considered together, some type of response can be mounted in Central Prince William Sound 90% of the time and 70% of the time at Hinchinbrook Entrance.
  - Mechanical Response is a more robust response technology than either dispersants or in-situ burning in both operating areas. Mechanical response is the response method least likely to be precluded by environmental conditions in both the Central Sound and Hinchinbrook Entrance areas.
  - Overall, response in either area is more likely to be precluded by environmental factors in winter than in summer.

Payne, J.R., A.A. Allen, *Use of Natural Oil Seeps for Evaluation of Dispersant: Application and Monitoring Techniques*, University of New Hampshire, Coastal Response Research Center, Durham, N.H., [http://www.crrc.unh.edu/final\\_payne02.pdf](http://www.crrc.unh.edu/final_payne02.pdf), 49 p., 2004.

Laboratory tests with the seep oil were conducted. Results from those tests indicated that the 11° API gravity seep oil from the Monterey Formation was not amenable to treatment with dispersants (0% dispersion), but similar tests on nearby Platform Holly produced oil (also from the Monterey Formation) indicated a possible dispersion of up to 70%. A limited set of *in situ* field tests (using a hand-held spray bottle with less than one pint of Corexit 9500) were completed

on the seep oils in June 2003 to determine if the earlier laboratory results were an artifact of the seep oil collection and shipment or some other unknown factor. The field tests convincingly demonstrated that the natural seep oils were not amenable to treatment with Corexit 9500.

Payne, J., *Field Notes and Critical Observations from the OHMSETT Heavy Oil Dispersant Trials October 13-16, 2003*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), Anchorage, Alaska, <http://www.pwsrcac.org/projects/EnvMonitor/dispers.html>, Note: has extensive appendices, but these are not included here, 64 p., December, 2006.

This report contains the transcriptions of tape-recorded notes and observations completed by James Payne of the 13-16 October 2003 heavy fuel oil dispersant tests at the OHMSETT facilities in Leonardo, New Jersey. Observations and recommendations for improvement are made.

Prince, R.C. R.R. Lessard, and J.R. Clark, "Bioremediation of Marine Oil Spills [Bioremédiation des pollutions maritimes pétrolières]", *Oil and Gas Science and Technology*, Vol. 58, pp. 463-468, 2003.

Biodegradation is noted as the eventual fate of oil spilled at sea that cannot be collected or burnt. Stimulating this biodegradation is thus an important option for maximizing the removal of oil from the environment, and minimizing the environmental impact of a spill. For handling oil while it is still floating on the sea surface, dispersants are thought to be advantageous because they maximize the surface area available for microbial attack, and stimulate biodegradation. If oil beaches on a shoreline, it is likely that biodegradation is limited by nutrients such as nitrogen and phosphorus, and the careful application of fertilizers stimulates the biodegradation of residual beached oil.

Resby, J.L., P.J. Brandvik, P.S. Daling, J. Guyomarch, and I. Eide, "Effects of Time on the Effectiveness of Dispersants – Final Report", SINTEF for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 116 p., 2007.

A test was performed to determine whether dispersants will remain with treated oil slicks over time and thus retain effectiveness. Dispersants were applied to 4 oils and then energy applied at later times in an IFP laboratory test. The effectiveness was found to depend very much on test conditions. The dispersant effectiveness did not correlate well with the surfactant content in oil. Limited leaching experiments with oil in ice were also conducted. No clear conclusions from these tests could be drawn.

Roberts, J. and L. Stevens, "Dispersant Effectiveness Testing: The New Zealand Experience", *Spillcon 2002*, Australian Institute of Petroleum, Sydney, Australia, 10 p., 2002.

This is a review of testing effectiveness in New Zealand. Testing was carried out on new products as well as existing stockpiles. Some age-related degradation was evident on older stockpiles.

Singsaas, I., T. Nordtug, J. Lise and M. Resby, *Strategy and Decision Model for Use of Dispersants on the Balder, Jotun and Ringhorne Oil Fields*, SINTEF Report TF80MK A05106 ISBN 82-14-03749-2, Trondheim, Norway, 2006.

This is a study of the potential of extending the use of dispersants on the Balder, Jotun and Ringhorne oil fields, as an alternative or supplement to mechanical recovery. The OSCAR model was used and showed that it is possible to respond to a fairly large blowout by use of dispersants. Extensive use of application close to the source may have a significant potential. Because of the continuous supply of fresh oil a dispersant action can go on for a long time in a blow out spill scenario provided that sufficient amount of dispersant is available. For a large instantaneous spill,

the usefulness of dispersants is restricted by the time window for effective use, and it is recommended to use dispersants in the initial phase, and mechanical recovery at a later stage.

SLR, "Dispersant Effectiveness Testing in Cold Water", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 43 p., 2002.

This study was a demonstration that dispersants can be a viable countermeasure operation in cold waters. A protocol for the testing of dispersant effectiveness, in open water, at the OHMSETT facility was developed in a previous project and this protocol was used in this project with minor modifications. The testing was completed at OHMSETT because the facility provides an opportunity to complete dispersant effectiveness testing at a large scale under controlled conditions. Hibernia and Alaska North Slope crude oils were used in the tests as these crude oils are produced and transported in cold waters. A total of twelve tests were completed with various combinations of oil type, dispersant type, and dispersant-to-oil ratios. From visual observations several combinations resulted in effective dispersion.

SLR, "Dispersant Effectiveness Testing on Alaskan Oils in Cold Water", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 86 p., 2003.

The objective of this study was to determine if Corexit 9500 and Corexit 9527 dispersants are effective in dispersing Alaskan crude oils in cold-water conditions at OHMSETT. Fourteen large-scale tests were completed at the OHMSETT facility with various combinations of oil type and dispersant-to-oil ratios. After each test the oil remaining in the containment area was collected and its volume determined. The chemically dispersed runs resulted in high percentages (75 to ~100%) of oil dispersing into the water column, with the exception of tests 10 (evaporated Northstar) and 14 (evaporated Endicott).

SLR, "Research on Powdered Activated Carbon to Remove Dissolved Oil Spill Dispersants from OHMSETT Basin Water", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 40 p., 2003.

Techniques to remove dissolved dispersant from OHMSETT water after the tank has been used for chemical dispersant experiments. The primary objective of the study was to develop and test a simple, inexpensive system for removing dissolved dispersant from tank water. The second objective of the study was to select and refine an analytical technique for determining the concentration of dissolved dispersant in the tank salt water. Powdered activated carbon (PAC) was determined to be the best answer for the removal of dissolved dispersant from the tank water after chemical dispersant tests at OHMSETT. A series of lab- and bench-scale tests were undertaken to quantify the expected performance of PAC and design a full-scale removal system. These tests concluded that: The adsorptive capacity of PAC for Corexit 9500A dispersant is about 1 g/g; A dose of 50 ppm PAC could adsorb 20 ppm of dispersant, and 20 ppm of PAC could adsorb 10 ppm of dispersant, even in the presence of up to 10 ppm of dispersed oil in the water; and The required contact time for the adsorption to proceed essentially to completion was 15 minutes.

SLR, "Spill Related Properties of IFO180 Fuel Oil", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 20 p., 2004.

The physical properties of IFO-180 are reported. These properties are relevant to the dispersion of this fuel.

SLR, "Spill Related Properties of IFO380 Fuel Oil", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 19 p., 2004.

The physical properties of IFO-380 are reported. These properties are relevant to the dispersion of this fuel.

SLR, "Dispersant Effectiveness Testing: Relating Results from OHMSETT at-sea Tests", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 91 p., 2005.

At-sea tests were conducted in the UK to estimate the viscosity of oil that limits chemical dispersion. This was accomplished by testing a number of intermediate fuel oils spanning a range of viscosities, up to a maximum of 7000 cP. Those tests showed that the limiting oil viscosity might vary with mixing energy. At the lowest wind speeds tested, the limiting oil viscosity in tests with the dispersant Corexit 9500 lay between the viscosities of IFO 180 (viscosity = 2075 cP) and IFO 380 (viscosity = 7100 cP). At slightly higher wind speeds (11 to 14 knots) dispersant effectiveness was near maximum with both oils and the limiting effect of oil viscosity was eliminated. Those tests were repeated at OHMSETT to determine whether OHMSETT tests could predict the oil viscosity limitations of dispersion observed at sea. In OHMSETT tests, wave energy also influenced dispersion performance. Tests conducted at 35 wave cycles per minute (cpm) produced far greater dispersant effectiveness than at sea and were discontinued. Tests in 33.3 cpm waves resulted in effectiveness that was similar to at sea, but subsequently proved to be slightly higher than at sea. Tests in 30 cpm waves produced no evidence of chemically augmented dispersion with any combination of oil or dispersant. In general, OHMSETT tests in 33.3 cpm waves appeared to produce somewhat higher levels of effectiveness than at sea for most combinations of dispersants and oils.

SLR, "Calm Sea Application of Dispersants", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 51 p., 2006.

The objective of the work described in this report was to determine the period of time for which the dispersants would remain with the oil in calm conditions and still be effective when the sea state increases and rapid dispersion can occur. OHMSETT tests showed that the oils would rapidly disperse when exposed to breaking waves after being left on a calm water surface for prolonged periods (up to 6 days for IFO-30 fuel oil or nearly 3 days for Ewing Bank 873 crude oil). There was no reduction in dispersant effectiveness that could be attributed to surfactant leaching at OHMSETT and there was no significant drop in dispersant effectiveness caused by evaporative loss from the crude oils causing an increase in oil viscosity, with the test oils and time periods used in this study. There was a single test using 50 L of oil (instead of 100L used in most tests) when the oil did not disperse after 66 hours and 44 hours, respectively, on the water surface. This was attributed to more movement and thus more contact with the water. The indications from the smaller-scale tests are that a significant drop in effectiveness, attributable to surfactant loss, can occur at much shorter time intervals of 12 to 24 hours when lower treatment rates (DOR of 1:50) of dispersant are used.

SLR, "Corexit 9500 Dispersant Effectiveness Testing in Cold Water on Four Alaskan Crude Oils", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 42 p., 2006.

The objective of the study was to complete effectiveness tests on Alaskan crude oils using Corexit 9500 dispersant and to compare the results to earlier experiments where Corexit 9527 dispersant was used. Four Alaskan crude oils were used in the test program. They were Alaskan

North Slope, Endicott, Pt. McIntyre, and Northstar and crude oils. Dispersant effectiveness was estimated by collecting the surface oil remaining on the tank surface immediately after the completion of the experiment and comparing the amount collected to that discharged at the beginning of the experiment. The Corexit 9500 dispersant was effective in all of the experiments and resulted in very high oil removal in all experiments.

SLR, "Dispersant Effectiveness Testing in Cold Water on Four Alaskan Crude Oils", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 59 p., 2006.

Dispersant effectiveness testing was carried out on four Alaskan crude oils. They were Alaskan North Slope, Endicott, Pt. McIntyre, and Northstar and crude oils. Dispersant effectiveness was estimated by collecting the surface oil remaining on the tank surface immediately after the completion of the experiment and comparing the amount collected to that discharged at the beginning of the experiment. The Corexit 9527 dispersant was claimed to be effective in all of the experiments and resulted in very high oil removal in all experiments.

SL Ross Environmental Research and Mar Inc., *Dispersant Effectiveness Testing on Viscous, U.S. Outer Continental Shelf Crude Oils*, U.S. Department of the Interior, Minerals Management Service, Herndon, Virginia, 16 p., January, 2006.

Twenty tests were completed at OHMSETT to test dispersant effectiveness on Harmony, Elly, Gilda, Gina, Irene and Heritage oils. These oils were all viscous oils from the U.S outer continental shelf. Oils of lower viscosity (about 600 cP) dispersed well, but higher viscosity oils did not. There was no dispersion in non-breaking waves at OHMSETT and there was no dispersion with almost all oils in the SL Ross wave tank. The exception was that the least viscous oil tested in the SL Ross tank showed some dispersion, while an oil of similar viscosity did not at OHMSETT.

SLR, "Dispersant Effectiveness Testing On Water-In-Oil Emulsions at Ohmsett", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 40 p., 2006.

Nineteen large-scale dispersant effectiveness tests were completed at the OHMSETT facility, on 'emulsions' of the same four oils used in the small scale testing. Emulsions for the large-scale tests were generated using two different procedures. There was no chemical or physical tests on the water-in-oil types to relate these to published literature criteria. The effectiveness values in OHMSETT ranged from about 0 to 35%. The dispersant effectiveness (DE) estimates from the OHMSETT tank tests are generally higher than those from the SL Ross tank. The higher DE values from OHMSETT are likely due to the higher wave energies that are achieved at OHMSETT.

SLR, "Dispersant Effectiveness Testing on Heavy OCS Crude Oils", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 21 p., 2006.

Twenty tests were completed at OHMSETT to test dispersant effectiveness on Harmony, Elly, Gilda, Gina, Irene and Heritage oils. These oils were all viscous oils from the U.S outer continental shelf. Oils of lower viscosity (about 600 cP) dispersed well, but higher viscosity oils did not. There was no dispersion in non-breaking waves at OHMSETT and there was no dispersion with almost all oils in the SL Ross wave tank. The exception was that the least viscous oil tested in the SL Ross tank showed some dispersion, while an oil of similar viscosity did not at OHMSETT.



SLR, "Chemical Dispersibility of OCS Crude Oils in Non-Breaking Waves", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 48 p., 2006.

Tests were completed to determine the chemical dispersibility, in non-breaking waves. In the SL Ross wave tank, using oils with viscosities ranging from 7 to 600 cP at 210 C, most of the oils showed little chemical dispersion in non-breaking waves.

SLR, "Investigation of the Ability to Effectively Recover Oil After Dispersant Application ", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 26 p., 2007.

This paper reports on a study to examine the recovery of dispersant-treated oils using conventional skimmers. Oleophilic and weir skimmers were able to recover dispersant-treated oil. In the oleophilic devices, water content was higher.

SLR, "Changes in Dispersant Effectiveness with Extended Exposure in Calm Seas ", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 27 p., 2007.

Dispersant effectiveness after water leaching was tested both in laboratory and at OHMSETT. It was observed that exposure to the higher water current speed of 13 cm/s, equivalent to a mean wind speed of 16.7 km/hr for 43 hours removed more surfactant than exposure to a water current speed of 5 to 6 cm/s, equivalent to a wind speed of 7.4 km/hr for 91 hours. Although the WSL (Warren Spring Laboratory test) effectiveness results gave an indication of the surfactant depletion process that was occurring in the tank tests, the relationship between WSL effectiveness result and behavior caused by exposure to breaking waves in the tank is not direct.

Smith, E.L., T. Galloway, A. Scarlett and M.N. Canty, "Potential Ecological Effects of Chemically Dispersed and Biodegraded Oils", University of Plymouth for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 52 p., 2005.

Mussels were exposed to oil and dispersed oil for 48 hours and then placed in clean water to observe the depuration. Amphipods were similarly exposed, but also in sediment. The dispersant, Superdispersant SD-25, did not affect the organisms to the same extent as Corexit 9527 did with Alaska North Slope oil. The experiments were replicated by the addition of bacteria. The experiments showed that chemically-dispersed oil impacts mussels and amphipods to a greater extent than undispersed oil, but there was recovery when the organisms were returned to clean water.

Sorial, G., S. Chandrasekar and J.M. Weaver, *Characteristics of Spilled Oils, Fuels and Petroleum Products: 2a. Dispersant Effectiveness Data For a Suite of Environmental Conditions-The Effects of Temperature, Volatilization and Energy*, EPA 600/R-04/119, United States Environmental Protection Agency, Research Triangle Park, North Carolina, 82 p., 2004.

Laboratory tests were conducted. A factorial experimental design was conducted for each of the three oils for four factors: volatilization, dispersant type, temperature and flask speed. Each of the four factors was studied at three levels except for the dispersant factor where only two dispersants were considered. Statistical analysis of the experimental data was performed separately for the three oils. Empirical relationships between the amount of oil dispersed and the variables studied were developed. The experiments showed that dispersal increased with mixing energy/flask speed for each experiment performed, although there were cases with overlapping ranges of dispersal for different flask speeds. In these cases, increases in dispersal due to lack of weathering or increased temperature evidently accounted for the overlap. In about half of the

experiments there was no significant relationship between weathering and dispersal. Where weathering was significant, it was inversely related to dispersal. In either case, the weathering affect was small compared to either flask speed or temperature. Dispersal did not show a consistent pattern with temperature increase. For most of the experiments, either the maximum or the minimum amount of dispersal occurred at the middle temperature of 22 °C.

Stone, T., "The Operational Use of Dispersants in the UK",. In *Oil Spill Symposium 2004: New Dimension in Oil Spill Response after the Prestige: Compensation and Response Technology*,. Petroleum Association of Japan, Tokyo, 13p., 2004.

The UK policies and approaches to the use of oil spill dispersants are summarized. Reviews of some past applications are presented.

Suidan, M.T. and G.A. Sorial, "Analysis of Dispersant Effectiveness of Heavy Fuel Oils and Weathered Crude Oils at Two Different Temperatures Using the Baffled Flask Test ", University of Cincinnati for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 28 p., 2005.

Swirling Flask tests were conducted on two heavy oils with Corexit 9500 as the dispersant. The test gave very poor results, dispersant effectiveness being less than 10% at a dispersant-to-oil ratio (DOR) of 1:10, mixing speed of 200 rpm, and a temperature of 16±1 °C. Under the same conditions the Baffled Flask Test (BFT) showed good dispersant effectiveness on both fuel oils. It was deemed that further tests with swirling flask would be fruitless. Further evaluations using the BFT to determine the effectiveness of three commercially available dispersants, Corexit 9500 (C9500), Super Dispersant 25 (SD25), and Agma on IFO 180 and IFO 380 oils were conducted. This report describes experiments to study the effect of different variables such as DOR, mixing speed, and temperature on dispersant effectiveness of these heavy oil products.

Trudel, K. and R. Belore, "Correlation of Ohmsett Dispersant Tests With At Sea Trials: Supplemental Tests", S.L. Ross for U.S. Minerals Management Service, Herndon, VA., <http://www.mms.gov/tarprojects/>, 16 p., 2005 .

Dispersant effectiveness tests for the Minerals Management Service project, "Dispersant Effectiveness Tests: Relating Results From OHMSETT to At-Sea Tests," (SL Ross et al., 2005) were completed at OHMSETT in October 2003. The primary objectives of the project were met, but two secondary objectives were only partly achieved:

- a) Measuring dispersant performance in the OHMSETT tank, with high dispersant-to-oil ratios (DORs) that had yielded high levels of effectiveness at sea; and
- b) Conducting replicate control runs for both test oils (IFO 180 and IFO 380) at wave frequencies of 30 and 33.3 cpm. This project addressed these two deficiencies.

The project involved a total of seven supplemental dispersion tests using IFO 180 and 380 fuel oils. Tests included: replicated controls; tests on IFO 180 and IFO 380 at high dispersant-to-oil ratios (DORs) in waves of 33.3 cpm; and tests on IFO 180 at high DORs in waves of 30 cpm. Control tests (no dispersant) with IFO 180 in 33.3-cpm waves provided a reliable estimate of oil losses by all means other than chemically augmented dispersion. These controls provided a baseline against which losses by chemically augmented dispersion could be compared. Oil recovery rates in control tests were 85% or greater, which showed that loss by "natural dispersion" and other sources in these tests were less than 15%. Tests of IFO 180 treated with Corexit 9500 (DOR of 1:25) in 33.3 cpm waves produced very high levels of effectiveness based on both visual assessment methods (visual 3 to 4) and direct measurement (6% recovered) confirming the result observed in the 2003 test. Tests with the more viscous, IFO 380 treated with

Corexit 9500 (DOR of 1:25) and tested in 33.3 cpm waves also yielded a high level of effectiveness both visually (visual = 3 to 4) and by direct measurement (15% recovered). The October 2003 test with IFO 380 with Corexit 9500 yielded ambiguous results. However, result of the present test is unambiguous and is consistent with the visual observations in the 2003 OHMSETT test, confirming that a high level of dispersion was taking place. Both of these observations were more consistent with the results of the at-sea tests in winds of 14 knots, where considerable dispersion was observed. They were consistent with the at-sea tests at 8 to 9 knots where little or no dispersion was observed.

The present tests of IFO 180 treated with Corexit 9500 in non-breaking waves (waves at 30 cpm) yielded apparently ambiguous results in that on the one hand, there was no visual evidence of dispersion, while on the other hand, amounts of oil collected at the end of the tests (50 and 69% of the oil recovered) suggested that significant chemically augmented dispersion had actually taken place. This inconsistency between visual observations and direct measurement is similar to observations in the 2003 study. The discrepancy appears to be due to artifacts of the test method. After treatment with dispersant, the oil is highly susceptible to dispersion, but there is clearly insufficient mixing energy in the waves to cause dispersion. However, localized turbulence caused by the oil collection tools during the collection phase of the run may have caused localized dispersion, thus accounting for the lowered levels of recovered oil. Apparently, for tests at low sea states, visual observations may be more reliable in estimating dispersion than measuring the oil remaining on the tank at the end of the test until test methods are improved.

Weaver, J.W., *Characteristics of Spilled Oils, Fuels and Petroleum Products: 3a.Simulation of Oil Spills and Dispersants Under Conditions of Uncertainty*, EPA 600/R-04/120, United States Environmental Protection Agency, Research Triangle Park, North Carolina, 90 p., 2004.

The EPA Research Object-Oriented (ERO) spill model is used to correlate the characteristics of oils and their chemical dispersability.

Wrenn, B.A., *Dispersion of Crude Oil and Petroleum Products in Freshwater*, EPA/600/R-08/037, United States Environmental Protection Agency, Cincinnati, Ohio, 33 p., 2008.

The objective of this research was to investigate the relationship between dispersion effectiveness in freshwater and the surfactant composition for fresh and weathered crude oil. Previous studies did not identify the dispersants that were investigated, nor describe the chemistry of the surfactants that were used. The absence of information on surfactant composition is a major impediment to the scientific investigation of dispersant effectiveness because this information is necessary for the development of a more fundamental understanding of dispersant effectiveness. Therefore, the relationship between surfactant chemistry and dispersant effectiveness was systematically evaluated. This report showed that, at least with Mars Blend crude oil in simulated lake water, dispersants can be designed to drive an oil slick into the freshwater column with the same efficiency as in saltwater as long as the hydrophilic-lipophilic balance (HLB) is optimum. Clearly, many more oils would need to be tested under different conditions (temperature, organic content, water composition, etc.) to enable firm conclusions that oil can be dispersed in freshwater as a response tool.





## **Appendix A   Comments on the Methodology and the Literature**

**Methodology** - Emphasis was placed on peer-reviewed literature in this report. Secondary emphasis was placed on papers in reviewed conference proceedings. The division of papers was on this same basis, ie. peer-reviewed papers, reviewed conference proceedings and then all others, or 'grey' literature. It should be noted that scientific quality does not reside only in the peer-reviewed literature and that there are some quality papers in the other two categories. There are perhaps also some questionable papers in the peer-reviewed literature. It should also be noted that several authors have similar papers in two or more of these categories. This is usually because their sponsor required a 'final' report and the authors also submitted a paper to a conference or a journal. Papers that could be summarized in groups, were. This is indicated by two references with one summary. If the papers were in a different category, the second summary is much shorter.

Papers that did not contain a significant amount of new information were summarized briefly. Many papers contain a lot of repetitive (to other papers) introductory material, as a necessity for their particular forum or venue. This introductory material was not repeated here.

**Comments** - The author has noted several points in preparing this summary:

1. Conflicts between findings between different papers are often attributable to different analysis techniques or approach.
2. Abstracts are for the most part reliable as a summary of the content of a paper. However, for some papers the abstracts do not correctly reflect the content of the paper and in a very few cases, were opposed to some of the internal data. In the latter cases, summaries prepared for this report, did not use the abstracts.
3. Several papers do not contain modern references. Unfortunately some authors relied on out-dated (sometimes by 30 years) references. In many cases this was inappropriate since there was new, verified, differing information. This reflects on the oil spill field, that often very poor literature searches are carried out.
4. Many authors over-use their own references, usually at the expense of other good references in the field.
5. There still exists a lot of poor methodology or analytical techniques. Sometimes these are a generation behind the current techniques.
6. Introductions to many of the papers are poor and contain many 'myths' and conventional statements rather than being an unbiased introduction to the topic.
7. Reviewed conferences, particularly IOSC, should use good review techniques. The scientific quality of some papers could be improved.