A Review of Literature Related to Oil Spill Dispersants

2011-2014

for

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Anchorage, Alaska

by

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PWSRCAC Contract Number - 955.14.02

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June, 2014

Abstract

This report is a review of the literature on oil spill dispersants published from 2011 to June 2014. The report identifies and focusses on recent advances in dispersant effectiveness, toxicity, and biodegradation. Other topics such as behavior and fate are also covered.

The prime motivation for using dispersants is to reduce the impact of oil on shorelines, but 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. Recent papers, however, confirm that inhibition is a matter of the surfactant in the dispersant itself and 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.

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. 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.

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 sometimes less than the toxicity of dispersed oil. Of the recent toxicity studies of dispersed oil, many researchers found that chemically-dispersed oil was more toxic than physically-dispersed oil. Some researchers found that the cause for this was the increased PAHs, typically about 10 to 100 times, in the water column. Others noted the increased amount of total oil in the water column. Few 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. 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.

Executive Summary

Overall

The literature on oil spill dispersants between 2011 and 2014 is extensive, consisting of more than 200 papers, which is the greatest number of papers in any such time period. The reason for this explosion of papers is, no doubt, the aftermath of the use of dispersants at the Deepwater Horizon spill.

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.

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. 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.

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 at sea so there is real information for assessment and modeling.

Effectiveness issues are confounded by the fact that various tests show highly different results depending on how they are constructed and operated. Detailed scientific examination of most of these show major deficiencies. Emphasis should be on 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.

Tank Testing

Tank testing continued 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, fluorometers were used. Studies show that because the amount and distribution of PAHs, the target compound for fluorometers, change with time during the course of a chemical dispersion event, a fluorometer can never be truly ‘calibrated’ for a particular oil and dispersant combination. The totally-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.

In summary of the many toxicological studies of water-accommodated fractions (WAF) versus chemically-enhanced water-accommodated fractions (CEWAF) the following generalizations can be made:

a) The results of the studies depend very much on the type of study, the species, life stage and the conditions of exposure and measurement,

b) Results may appear to be variable, however there certainly are patterns emerging in the results,

c) For some species and some measurements the toxicity of the CEWAF was about the same as the WAF at the same concentrations, however it must be borne in mind that the concentrations of CEWAF would be 10 to 100 times that of the WAF for an effective dispersion,

d) In other studies, it was found that CEWAF was from slightly to 1.5 to 4 to 100 to 300 times more toxic than the WAF,

e) Some studies showed that the CEWAF toxicity was as a result of the increase of PAHs compared to WAF which has much less PAHs. The PAHs sometimes corresponded to the toxicity increased shown in c) above.

f) In some studies, CEWAF was shown to be somewhat cytotoxic and genotoxic, and

g) There appear to be some species or life stages that are sensitive to CEWAF and less sensitive to WAF.

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

Biodegradation of Oil Treated by Dispersants

The results of these biodegradation studies are summarized as follows:

a) Biodegradation depends on the conditions of the tests, the species of microbial agents chosen and the nutrients available,

b) In older studies noted about, more than half of the researchers noted inhibition of oil biodegradation by dispersants and the others found that biodegradation rates were about the same. In the current literature time period about one-third of studies noted inhibition of oil biodegradation, about 1/3 noted acceleration and about 1/3 of studies noted that the rates were the same. and

c) None of the studies included specialized techniques to observe the separate degradation of alkanes and PAHs as suggested by the National Research Council (Committee, 2006).

Monitoring Dispersant Applications

The most common protocol at this time is the 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. Since the use of dispersants and dispersant monitoring at the Deepwater Horizon, there has been a review of the protocols and several deficiencies have been noted and improvements to the existing protocols have been suggested. The visual guides now available, require improvement and do not really show what an effective nor an ineffective dispersion looks like. The use of fluorometry is also now being questioned as fluorometers respond only to the smaller PAHs, whose concentrations in the water are greatly enhanced by the use of dispersants. The traditional use of a ‘SMART ratio’, the ratio of the concentration of the slick after dispersants are applied and the background concentration, is under scrutiny. This ratio was traditionally accepted as 5 but was taken as 1.5 and 3 in the Deepwater Horizon spill. Many different types of monitoring were carried out during the Deepwater Horizon spill, including water sampling and analysis of various types, measurement of dispersant components in the water, biological testing, etc. In addition, the application of dispersants at depth had resulted in subsea monitoring. Many results are presented on improvements suggested as the monitoring carried out during the Deepwater Horizon spill.

Dispersant Use in Recent Times

Dispersant use in recent times is dominated by the application at the Deepwater Horizon spill. Unfortunately no assessments of effectiveness under aerial application were carried out nor could quantitative assessments of the subsea application be 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 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.

Weather and Application of Dispersants

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 areas such as in Prince William Sound.

Subsea Application and Subsea Behavior

During the Deepwater Horizon spill extensive subsea use of dispersant was made. The effects of this on the fate of oil is complicated by the natural behavior or subsea blowouts which generate subsea plumes without the use of dispersants. Such situations are too complex to determine the actual contributions of the dispersants.

Monitoring Application Using Dispersant Components

Dioctyl sulfosuccinate (DOSS) is a major component of the Corexit dispersants and has an aquatic toxicity of approximately double that of the dispersant itself and this component can be monitored separately in the water column. Some groups also studied the use of dipropylene glycol n-butyl ether (DPnB), a solvent component of Corexit dispersants, as a possible marker for the fate and effectiveness of oil dispersion after the Deepwater Horizon spill. The question in both cases is how these two compounds partition between oil, water and dispersed oil. As this factor is unknown, there is not much to be gained by monitoring these compounds.

Human Health Aspects

For the first time, there were studies on the effects of dispersant application on humans. Tests of inhalation models showed that there might be a concern over human inhalation of dispersant vapors, however the exposures and the levels of exposures may not be pertinent to at sea applications. Further study is needed.

Recommendations for Further Research

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
BOEM – Bureau of Ocean Energy Management
BSEE – Bureau of Safety and Environmental Enforcement
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
DOSS - Dioctyl Sulfosuccinate, one of the surfactants in Corexit dispersants
DPnB - Dipropylene glycol n-butyl ether, a component of Corexit dispersants
DWAF - Dispersed Water-Accommodated Fraction - The sum total of oil in a water sample including chemically and physically dispersed and soluble oil
DWH - Deepwater Horizon, also known as the Macondo spill
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
GC-MS – Gas Chromatography-Mass Spectrometry
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^{o}C
LC – Lethal Concentration
LC50 or LC$_{50}$ - Lethal concentration to 50% of the test population
LDH - lactate dehydrogenase - an enzyme that is measured and an indicator of stress in an organism
LISST – Laser In-Situ Scattering and Transmissometry - a brand of particle measuring instrument
LOEC - Lowest Observable Effect Concentration - the lowest concentration that produces a noted effect
Microtox - A simplified toxicity measuring system using light-emitting bacteria
NAS - (U.S.) National Academy of Sciences
NOAA – National Oceanic and Atmospheric Administration
NRDA – Natural Resources Damage Assessment

NOEL - No-Effect Level
OMA - Oil Mineral Aggregates
PAH – Polycyclic Aromatic Hydrocarbon(s)
∑PAH - the sum of PAHs in a given sample
PWSRCAC - Prince William Sound Regional Citizens' Advisory Council
QA – Quality Assurance
QC – Quality Control
SERVS - Ship Escort Response Vessel System - A division of Alyeska providing response services in Prince William Sound
SMART ratio - The ratio of hydrocarbons measured under a slick before and after dispersant application - the ratio of 5 was used in the past to declare a dispersion effective, during the Deepwater Horizon Spill, a ratio of 1.5 or 3 was used, probably should be 10 or more
SMART - Special Monitoring of Applied Response Technologies
SPM - Suspended Particulate Matter
TPAH - Total Petroleum Aromatic Hydrocarbons
TPH - Total Petroleum Hydrocarbons - a measure of total hydrocarbons in a sample, usually by GC - FID
UV - Ultra-violet light, a high frequency (past violet) portion of light spectrum
VMD – Volume Mean Diameter, the diameter of which accounts for ½ volume of particles
VOC - Volatile Organic Carbon - fraction of hydrocarbons which evaporate readily
WAF - Water-Accommodated Fraction - The sum total of oil in a water sample including physically dispersed and soluble oil

Acknowledgements

The author thanks Joe Banta of the Regional Citizens' Advisory Council of Prince William Sound, the contract manager for this project.

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1. Introduction

1.1 Objectives

The objectives of this review are to summarize the literature from 2011, including the last report (2008), to the current date (2014) 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 2011. As such it covers all known dispersant-related literature from that time period to June of 2014. A wide-ranging literature search was carried out and included literature from all known sources. More than 200 pieces of literature were found. Of these, 80 were found to be unique and included new findings which are summarized here. Several papers are by the same author and were summarized together. Papers covering the same topic with the same findings were grouped together.

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 report's recommendations.

2 Overview of Dispersants

The use of dispersants still generates debate four decades after the 1967 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; and reduce the impact on birds and mammals. 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.

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 and 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.

Since the second dispersant review in 2008, not much has changed on the effectiveness front other than tank test results disagree with the field trial results in the 1990's. There is much evidence to show that the current tank tests are not conducted using the recommended procedures and analytical methods.

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 should 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. Long-term effects of chemically-dispersed oil are poorly-studied and relatively unknown at this point in time. Again little has changed from the first review in 2002, but it is very clear now that the toxicity of dispersed oil is greater than that of physically-dispersed oil, primarily because of the large increase (5 to 50 times) the amount of aromatics and PAHs in the water column.

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), moreover 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 must remember that any dispersion is temporary and effectiveness measures should always relate this to the time after dispersant application that the measure was taken.

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 larger amounts 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. In the late 1990's emphasis was focussed on laboratory and field tests. Currently, the only extensive work is being carried out in tanks.

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 effect 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, several workers have noted that there are several important principles of experimental design which are often ignored including systematic errors which effect 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.
In the past twenty years, offshore trials have been conducted in the North Sea primarily by Great Britain and Norway (Fingas, 2002). Similar trials were also conducted in the 1980s in France and North America. Several papers have assessed the techniques used to measure effectiveness in these tests. 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. This is based on questionable analytical methodology. Ideal methodology may result in even smaller values, however, the results are not predictable at this time. The validity of older test results is even more questionable because of both the analytical methodology and data treatment methods (Fingas, 2002). It is interesting that the percentage values assigned to all field tests ever conducted, average 19%, both in the older and more recent field trials.

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 not valid forms of analysis and are no longer used. Fluorometry has been used as well for the last 20 years, 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. It is impossible to calibrate fluorometers for whole oil dispersions in the laboratory, instead one should use accurate techniques such as extraction and gas-chromatographic analysis. It is also known that the aromatic ratio of the oil changes as a result of the dispersion process.

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 of hydrocarbons, 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 and Ka'aihue, 2004).

The effectiveness determined during field trials varies significantly. Results (from about 1994), 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).

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. Furthermore, the half-life of the oil in the water column was typically not measured, despite the fact that at several field trials, oil was observed to be resurfacing (Fingas et al., 2003).

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 et al., 1995). 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. About 15 years ago, there were more tests, but these have largely disappeared.

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 et al., 1995).

Fingas (2005) calculated 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 were compared in several laboratory vessels under several energy conditions.

3.1.3 Tank Tests

Tank tests continued during this literature review period. 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. 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 NAS 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. 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.

The following are 17 critical factors that need to be considered in any test for measuring the effectiveness of dispersants in a tank (Fingas and Ka'aihue, 2004):

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 up to over 80%. In one set of experiments, some researchers 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 as dispersants cause changes in oil behavior 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. There is further discussion on analytical techniques in a section below.

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.

5.Time lag and length of time plume followed - There is a time lag of 15 to 90 minutes before maximum dispersion takes place. Because of resurfacing of oil, the plume loses oil over 2 days.

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.

9.Behavior of oil with surfactant content - Oil with surfactant content behaves differently than oil without surfactant. 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 and 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.
15.Heterogeneity of slick and plume - Neither the slick nor the plume are homogeneous in distribution and concentration. Measurements over small spatial areas and correct use of the data will improve the quality of the results.
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 Methods

Analytical methods continues to be a major concern. It should be made very clear that only high-quality GC/MS techniques produce a true quantitative means (Fingas, 2011a). Studies show that because the amount and distribution of PAHs, the target compound for fluorometers, change with time during the course of a chemical dispersion event, a fluorometer can never be truly ‘calibrated’ for a particular oil and dispersant combination. The composition of the oil changes with respect to aromatic content as it weathers and is dispersed, with the concentration of aromatics increasing. A fluorometer 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, however there needs to be more recognition that this method will always be relative and highly prone to error.

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.

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, 2011a). Oil does neither of these two things. Oil is a mixture of dozens to hundreds of compounds, none with a chromophore, a 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 1967 caused massive damage to intertidal and sub-tidal life (Fingas, 2011a). 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 lethal 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 themselves as 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 maybe 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 (Fingas, 2011a). 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 oil was diesel fuel, which disperses naturally under high sea conditions.

Sensitivity to dispersants and dispersants varies significantly by species and life stage. Embyronic and larval stages are more sensitive than adults to both dispersants and dispersed oil. 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 lack of longer-term studies on the toxicity of dispersants themselves.

If the dispersants are effective there is a large increase in the amount of hydrocarbons in the water column. The important factors in monitoring the plume are the measurement of the elevation of hydrocarbons at depth in the water column. Clues on what these hydrocarbon increases as a result of dispersant application might be, can come from several laboratory studies. A study by Gardiner et al. (2013) included the measurement of compounds in naturally and chemically-dispersed compounds in Alaska North Slope Crude. Table 1 shows the results. The ratios of the compounds in the chemically-dispersed to naturally-dispersed are shown in the right hand columns of the table. In this case, the PAHs were approximately, 40 to 120 times greater in the chemically-dispersed mixture. Similarly a study by Rowe et al. (2009) showed that the ratio of PAHs in the chemically dispersed oil ranged from 2 to 25 times that of the naturally dispersed oil. This is shown in Table 2. It should also be noted that compounds in the dispersant also show a PAH signal by this type of analysis. This was also noted in a study by Zuijdgeest and Huettel (2012). The amount of PAHs released after the applications by dispersants were an average of about 10 times higher than for naturally dispersed oil. The increases in PAHs may account for the toxicities seen in toxicity tests.

Table 1 Values of TPH and TPAH from a Laboratory Experiment

(from Gardiner et al., 2013)

				Ratios	
Class	**WAF**	**BWWAF**	**CEWAF**	**CEWAF/WAF**	**CEWAF/BWWAF**
TPH	1.95	6.51	379	194	58
TPAH	0.067	0.191	8	119	42
sum parent PAHS	0.034	0.069	1.03	30	15
Sum Alk PAHs	0.033	0.122	6.97	211	57
Parent Napthalene	0.03	0.058	0.334	11	6

WAF - Water Accommodated Fraction (equivalent to natural dispersion)
BWWAF - Breaking Wave Water Accommodated Fraction
CEWAF - Chemical Enhanced Water Accommodated Fraction (equivalent to (chemically-dispersed)

Of particular concern is the actual toxicity of the dispersed oil - compared to physically-dispersed oil. Most modern toxicity studies address the problem as a comparison between these two aspects.

Table 2 Values of TPH and TPAH from a Laboratory Experiment

(from Rowe et al., 2013)

Starting Stock	Concentration mg/L	Ratio CEWAF/WAF
Control	0	
Dispersant	1	
WAF low	6.7	2
WAF High	43	7
CEWAF low	13	(2 to 45)
CEWAF high	302	

The toxicity studies in the period of 2011 to 2014 are shown in Table 3. There are more than 40 studies noted. This is the most in such a short time period and this abundance is no doubt the result of the Deepwater Horizon spill which attracted a large amount of interest.

Table 3 Summary of Toxicity Studies

Species or Class	Effect of Dispersants	Author	Year
atlantic herring embryos	same at same concentration	Adams et al.	2014
rabbit fish	100-fold more toxic	Agamy	2013
rabbit fish	slightly more	Agamy	2012
rabbit fish	same	Agamy	2012
microzooplankton	significantly increased	Almeda et al.	2014
copepods	1.6 times more toxic	Almeda et al.	2014
mexozooplankton	2.3 to 3.4 times more toxic	Almeda et al.	2013
juvenile mud crabs	significantly increased	Anderson et al.	2014
Spotted sea trout	larval more, juvenille less than high mixing	Brewton et al.	2013
european sea bass	lowest growth rate of all types of exposures	Claireaux et al.	2013
marine copepod	same but dispersant alone shows more lethality	Cohen et al.	2014
tambaqui - tropical fish	dispersant and CEWAF causes impairment to gill ion regulation	Duarte et al.	2010
arctic marine amphipod	dispersants decreased lysomal stability	Faksness et al.	2011
mallard duck eggs	variable but dispersant appeared to increased transference of compounds into eggs	Finch et al.	2012
Marine plankton	little effect	Gao et al.	2014
Coral larvae	CEWAF led to less settlement and Dispersant alone to least settlement	Goodbody-Gringley et al.	2013
Northern algae and copepods	dispersants toxic	Hansen et al.	2014
copepod	increased toxicity at low levels, decrease at high levels	Hansen et al.	2012
shrimp and silverside	dispersant alone slightly toxic, same as mixture	Hemmer et al.	2011
diatom	exposure to dispersants or DEWAF caused membrane damage	Hook et al.	2012
Genotoxicity and endocrine disruption	only very little toxicity noted with some products	Judson et al.	2010
estuarine fish	dispersant exponentially increased PAH concentrations, CEWAF more toxic than WAF	Kuhl et al.	2013
pelagic tunicates (zooplankton)	dispersant increased ingested oil, but this was eliminated via fecal pellets	Lee et al.	2012
Pacific Oyster	Imune and detoxification affected negatively by chemical dispersants	Luna-Acosta et al.	2011
Mullet	about the same toxicity	Milinkovitch et al.	2013
Mullet	about the same toxicity	Milinkovitch et al.	2012
Fish, Lisa ramada	CEWAF more toxic	Milinkovitch et al.	2011
Mullet	dispersant application likely to impair cardiac function	Milinkovitch et al.	2013
Arctic cod	dispersants do not appear to have transcriptional effect	Olsvik et al.	2012

Table 3 ctd. Summary of Toxicity Studies

Species or Class	Effect of Dispersants	Author	Year
elegans (worm)	dispersants cause genetic aberations	Polli et al.	2014
Sargassum (aquatic plant)	dispersants caused more sinking than oil alone	Powers et al.	2013
bacterium, Nitrosomonas europaea	no difference in toxicity	Radniecki et al.	2013
sea urchin embryos	Some dispersants showed toxicity	Rial et al.	2014
chironomid larvae	some dispersants showed toxicity	Rotimi et al.	2011
Top Smelt	CEWAF led to mortality	Van Scoy et al.	2012
Salmon smolts	Dispersed and undispersed led to similar metabolic profiles	Van Scoy et al.	2010
seagrass	more physiological impact with dispersant	Wilson et al.	2012
sperm whale skin cells	dispersants were cytotoxic and genotoxic to sperm whale skin fibroblasts	Wise et al.	2014
mallard duck eggs	dispersants were found to be embryotoxic when applied to duck eggs	Wooten et al.	2012
rainbow trout embryos	chemical dispersion increased toxicity dramatically, by >35 to >300-fold, consistent with the increase in PAHs	Wu et al.	2012
Caenorhabditis elegans	dispersant-oil mixture induced more significant effects than oil or dispersant-alone, also this induced genetic changes	Zhang et al.	2013
mammalian cells	experimental results show changes in intracellular oxidative radicals leading to mitochondrial dysfunctions and apoptosis	Zheng et al.	2014

In summary of the many toxicological studies of water-accommodated fractions (WAF) versus chemically-enhanced water-accommodated fractions (CEWAF) the following generalizations can be made:

a) The results of the studies depend very much on the type of study, the species, life stage and the conditions of exposure and measurement,

b) Results may appear to be variable, however there certainly are patterns emerging in the results,

c) For some species and some measurements the toxicity of the CEWAF was about the same as the WAF at the same concentrations, however it must be borne in mind that the concentrations of CEWAF would be 10 to 100 times that of the WAF for an effective dispersion,

d) In other studies, it was found that CEWAF was from slightly to 1.5 to 4 to 100 to 300 times more toxic than the WAF,

e) Some studies showed that the CEWAF toxicity was as a result of the increase of PAHs compared to WAF which has much less PAHs. The PAHs sometimes corresponded to the toxicity increased shown in c) above.

f) In some studies, CEWAF was shown to be somewhat cytotoxic and genotoxic,

g) There appear to be some species or life stages that are sensitive to CEWAF and less sensitive to WAF, and

h) 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.

3.2.1 Toxicity of 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 typically less than the toxicity of dispersed oil. There are few 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.

The test results of dispersant toxicity alone are sometimes included in the studies shown in Table 3. The results of the dispersant alone toxicity studies can be summarized as:

a) The results of the studies depend very much on the type of study, the species, life stage and the conditions of exposure and measurement,

b) Results may appear to be variable, however there certainly are patterns emerging in the results,

c) For some species and some measurements the toxicity of the dispersant was about the same as the oil at the same concentrations,

d) In other studies, it was found that dispersant was more toxic than the WAF or oil alone,

e) In some studies, dispersant alone was shown to be somewhat cytotoxic and genotoxic, and

g) There appear to be some species or life stages that are sensitive to dispersant and less sensitive to WAF.

3.2.2 Photo-enhanced Toxicity

Several researchers have noted that oil and especially dispersed oil has greater toxicity when exposed to UV or UV components of natural sunlight (Fingas, 2008). In the time period of this literature study there were no specific tests on this facet of toxicity.

3.2.3 Testing Protocols

A group of scientists developed protocols known as CROSERF (Chemical Response to Oil Spills: Ecological Research Forum) (Coehlo et al., 2013). The CROSERF aquatic testing protocols were developed with the objective of standardizing test methods and reducing inter-laboratory variability. 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.

3.3 Biodegradation

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. 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 affect 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. 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. 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. Perhaps 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).

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(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.

Another issue is the measurement of biodegradation. Several recent studies have shown that the use of simple gas chromatographic techniques for measurement are inappropriate (Fingas, 2014a; Aeppli et al., 2012). It has been shown that oil that has undergone biodegradation or photooxidation, contains oxygenated compounds. The end products of biodegradation include acids, esters, ketones and aldehydes. Some of these compounds cannot be analyzed by standard extraction and gas chromatographic methods. Conventional methods do not analyze for polar compounds and would not count them in the analytical results. Studies have shown that highly oxidized oil, including that undergoing biodegradation and photooxidation, is not properly analyzed by conventional techniques. Conventional analytical techniques may miss as much as 75% of the oil mass. Conventional techniques may overstate biodegradation by as much as four times.

Table 4 summarizes the new studies carried out in the review period.

Table 4 Studies on Biodegradation 2011-2014

Type	Result	Detail	Author	Year
laboratory	same rates with or without dispersant	Colwellia sp. Primary degraders	Baelum et al.	2012
laboratory	surface culture degraded DOSS, but cryo culture had lag of 28 days	observe the effect of DOSS on oil degradation	Campo et al.	2013
Others Laboratory	accelerated rates with dispersant	largely a literature review	Chakraborty et al.	2012
Indirect assessment	extensive DO loss in spill area	measured DO	Du et al.	2012
Laboratory	Dispersant toxic to some species of hydrocarbon-degrading bacteria	Toxicity tests on isolates from LA shoreline	Hamdan et al.	2011
Laboratory	No difference between degradation with or without dispersant	tests on sediment columns	Macias-Zamora et al.	2014
Laboratory	Dispersants appeared to increase biodegradation somewhat	Questionable analytical techniques	McFarlin et al.	2011
Laboratory	No difference without and with dispersant	Pseudomonas aeruginosa was biodegrading organism	Moersidik et al.	2013
Mesocosm	Addition of dispersant or dispersed oil inhibited ciliates and transfer of carbon up the food chain	biomass of ciliates in mesocosm was measured as a function of inputs	Ortmann et al.	2012
Laboratory	dispersant significantly inhibited denitrification, but stimulated organic matter mineralization	marsh sediment incubated	Shi et al.	2014
Laboratory	Photooxidation and dispersants may have increased degradation of alkane components	Using fluorescence techniques	Zhou et al.	2013
Laboratory	Variable results dependent on type of dispersant	growth rate of isolated bacteria and fungi in incubated field samples	Zolfaghari-Baghbaderani et al.	2012

The results of these biodegradation studies are summarized as follows:
a) Biodegradation depends on the conditions of the tests, the species of microbial agents chosen and the nutrients available,
b) In older studies noted about, more than half of the researchers noted inhibition of oil biodegradation by dispersants and the others found that biodegradation rates were about the same. In the current literature time period about one-third of the studies noted inhibition of oil biodegradation, about 1/3 noted acceleration and about 1/3 of the studies noted that the rates were the same, and
c) None of the studies included specialized techniques to observe the separate degradation of alkanes and PAHs as suggested by the National Research Council (Committee, 2006).

4 Other Issues

4.1 Dispersant Use in Recent Times

Dispersant use in recent times has been dominated by the extensive use of dispersants at the Deepwater Horizon spill (Nedwed, 2013). Dispersants were used at the well head and on the surface. Many of the studies summarized in this report are as a result of the Deepwater Horizon spill and the use of dispersants there.

4. 2 Monitoring Dispersant Effectiveness

The extensive monitoring carried out at the Deepwater Horizon spill resulted in a thorough review of monitoring protocols (Fingas and Banta, 2014). The result of this review addresses several issues with the existing protocols pointing the way to improvement. Some these are noted below:

Purpose: The prime purpose of monitoring after a dispersant application is to determine effectiveness. In recent years other objectives have been added to this, including a preliminary assessment of environmental effects, definition of the dispersed oil plume and determination of the time extent of the plume.

Overview: The monitoring of the slick is to establish whether or the hydrocarbons in the water are dispersed oil and whether they are elevated enough to constitute an effective dispersion. Since dispersions decline with time, the assessment should include a time factor. The plume usually forms after half an hour and a half-life of the plume may be 12 to 36 hours. There are several false indications, primarily the fact that dispersion releases many PAHs, which fluorometers only respond to. A high fluorometer reading does not necessarily indicate high dispersion. Data suggest that fluorometer readings are sometimes unreliable but should be 10 to 50 times higher in the dispersed plume than under a naturally dispersed plume. Further, dispersant alone does give a fluorometer signal.

Standards: The use of standards for these measurements must be implemented. There exist standards for many phases of spill monitoring. These include standards from EPA, ASTM and ISO. Currently, many of the monitoring protocols have not used standards.

Discussions on SMART: Several papers have noted that there are difficulties with some of the instruments traditionally used in SMART monitoring. Instruments such as the flow-through fluorometer should be replaced, perhaps with an in-situ particle measuring instrument.

SMART ratio: This is the ratio of increase which should be shown in fluorometric readings between background and dispersed slick. The current standard is an increase of 5 over background readings. Ratios of 1.5 and 3 were used at the Deepwater Horizon spill. It is clear from the literature that a ratio of at least 10 or more would be more scientific and appropriate.

Length of Time Sampled: A short-coming of current protocols is that they do not consider the normal de-stabilization of dispersed oil in the water column. Dispersed plumes should be

monitored for at least 6 hours and if possible, marked plumes should be measured the next day (e.g. 24 hours). This truly indicates the longer-term effectiveness of the dispersion.
Fluorometers: It is clear that fluorometers only measure the smaller PAH compounds and thus cannot be calibrated to read total oil concentration. The composition of the oil changes with respect to aromatic content as it weathers and is dispersed, with the concentration of aromatics increasing in the latter case. Thus the apparent fluorescent quantity increases in the dispersing process. There are differences in how fluorometers respond and some appear to over-respond to PAHs as a result of dispersion. Fluorometers also respond to dispersants alone. Fluorometers, at best, give a relative reading. Furthermore fluorometers require frequent checking, cleaning and adjustment.

Water Sampling and Analysis: Water sampling and analysis are necessary, at least every hour or so to ensure that the fluorometers and particle size measuring instruments are still working properly. Further the analysis of TPH, alkanes and PAHs provides essential information on the nature of the dispersion. Field sampling should be carried out using available standards and with appropriate equipment.

Particle Size Measurement: Particle size created as a result of dispersant action is a good indicator of effectiveness. The new generation of particle size instruments is quite capable of providing reliable readings in-situ. Particle or droplet sizes are typically measured as Volume Median Diameter (VMD). This is the size at which half of the volume is accounted for and is an accurate representation of the bulk of the droplets. A VMD less than 50 µm, has historically been accepted as an indication that the dispersion is chemically-enhanced and is effective. Larger VMDs are an indication that the dispersions are unstable and will separate faster than an effective dispersion. In addition, new models of particle size measurement devices can integrate droplets to provide an indication of total oil. This measurement appears to be more reliable than fluorometers for estimating the total oil under a slick and in a plume.

Particle size measuring devices typically respond to particles of any origin. The same particle size analyzer as used for oil measurement may also be used for measuring gas bubbles and sediment particles in water. One way to be assured that the particles one is measuring are oil, is to run a fluorometer alongside the particle measuring device to assure that the high number of particles is indeed oil-related.

Particle vs. Dissolved Portion: Several scientists have noted that separately measuring the particles from the dissolved portion is necessary to understand dispersion. This can be accomplished by using particulate filters and analyzing the filter separate from the dissolved oil which passes through the filter.

Depth of Monitoring: The SMART protocol currently states that fluorometry is carried out at depths of 1 meter and 10 meters. These are felt to be inappropriate in that 1 meter is too shallow and with the usual depth error, this sample will often be taken near the surface. A top depth of 2 meters is felt to be much more appropriate. Ten meters is too deep and little oil is actually at that depth at any stage of dispersion. A bottom depth of 5 meters is suggested. Further, it is clear from the data that there may be contamination in the lower sample which was carried through from sampling upper layers. This is discussed in the next section.

Decontamination of Sampling Equipment: Oil clings to tubes and equipment resulting in subsequent erroneous readings. Sampling equipment cannot be moved from upper to lower sampling. The higher concentrations at the upper levels will contaminate the equipment and tubes and result in apparent high levels at depth. Further all equipment should be decontaminated after runs to ensure there is no carry-through. Protocols for decontamination require development and implementation.

Water Samples: Water samples are taken to provide confirmation of on-site measurements as well as to provide further information on the seawater and the dispersion. Typical analysis involves measurement of total petroleum hydrocarbons (TPH), PAHs and alkanes. Specifically GC-MS analysis includes aliphatic hydrocarbons, monocyclic (e.g., benzene, toluene, ethylbenzene, and xylene up to C3-benzenes), polycyclic, and other aromatic hydrocarbons (PAHs) including alkylated homologs (e.g., 2-, 3-, and 4-ring PAHs (C0-C4-naphthalenes, C0-C3-fluorenes, C0-C3- dibenzothiophenes, C0-C4-phenanthrenes-anthracenes, C0-C4-naphthobenzothiophenes, C0-C2-pyrenes-fluoranthenes, C0-C4-chrysenes, and the pyrogenic PAHs)), and hopane and sterane biomarker compounds, TPH, and volatile organic compounds.

Monitoring of the Dispersant Constituents: Several groups monitored dispersant constituents during the Deepwater Horizon spill. This included the solvent, dipropylene glycol n-butyl ether (DPnB) and the surfactant, Dioctyl Sulfosuccinate (DOSS). While this may appear to be a valid technique, there is a problem that these constituents probably have separated from the bulk of the dispersant and perhaps from the oil. This is especially the case for DOSS which is highly water-soluble while the other two surfactants in Corexit dispersants (Tweens and Spans) are not so.

Monitoring Biological Effects: Several parties monitored the field toxicity of dispersed oil. The Microtox test is a proxy for aquatic testing and can be carried out within minutes. It uses photoluminescent bacteria (*Vibrio fisheri*) to assay toxicity. A field version of this test is available. The QwikLite assay uses light emission from the dinoflaggellate *Pyrocystis lunula*, to provide a rapid proxy of phytoplankton toxicity. The Microscreen Mutagenicity test uses a λ-containing lysogenic strain of *Escherichia coli*, to act as a rapid test for mutagenicity. The latter-two tests require a longer time and a small shipboard laboratory.

Use of Chemical Indicators to Assess Biological Effects: The USA EPA established benchmark levels of concern for PAHs in water and sediment to screen for potential adverse impacts to aquatic life. For these benchmarks, a total of 41 oil-related PAH compounds were assessed jointly through a mixture approach because they have a cumulative effect on aquatic organisms. These compounds include 7 volatile organic compounds, 16 parent PAHs and 18 alkylated homologues of the parent PAHs. The individual compounds are given potency divisors, which are used in calculating the cumulative toxicity of the mixture of compounds in each sample known as the acute or chronic aquatic life ratio. These are used in place of actual biological measures but are based on extensive laboratory data.

Dissolved Oxygen Measurement: Dissolved oxygen measurement can indicate biodegradation, however this would not occur on a short term basis. Measurement of dissolved oxygen at the time of the dispersion would serve as a background only for future measurements in the same area. At depth, this might serve as an indicator, however as methane degrades rapidly, dissolved oxygen is only an indicator of the extent of methane biodegradation.

Data Issues: A universal complaint from users of any monitoring protocol was that there were no protocols or systems for the organization or delivery of data. Most of this derives from operations during the Deepwater Horizon. In small operations this may not be as much of an issue. Data handling is certainly an issue.

Visual Monitoring: Visual monitoring is to be carried out by most dispersant monitoring protocols. The monitoring focusses on the major phenomenon that an effective dispersion is to have a coffee-colored plume. This is not to be confused with a whitish plume, which is dispersant only. Further, dispersant running off an oil slick can leach some material giving a slightly brown coloration in certain parts. This is not to be confused with a dispersed oil plume. Unfortunately the visual guides in the past are not adequate to guide visual observers in judging effectiveness.

Quality Assurance: Currently SMART and other protocols do not have a quality assurance program associated with them. QA/QC should be a requirement for all phases or tiers of a monitoring program. Analysis should be carried out with certified procedures, certified chemists and in certified laboratories (3C's).

Field Effectiveness Tests: Only a couple of dispersant monitoring protocols advise a field test. A field test consists of taking a small sample of the oil directly in the field, applying dispersant and then gauging the result. This is useful as this provides a direct means of estimating dispersant effectiveness. If it does not work in the bottle, it won't work on a real slick.

Monitoring Subsurface Plumes: Although some guidance on this was provided in recent times, this is really a topic for the deep sea oceanographers. This sample is complex and involves specialized equipment held only by experienced oceanographers.

Tracking Surface Plumes: Two buoys have shown the capability of tracking surface plumes as verified by several field tests, these are the Orion and Novatech devices. More than 30 devices or buoys were tested and none of the others complied with oil spill movement.

Tracking Subsurface Plumes: The Davis Drifter is purported to track subsurface or dispersed oil plumes, although there is no documented test of this.

Background Measurements: One of the problems is that sometimes measurements are to be made in situations where there is little background information. Compounding that, there may be dispersant application in areas where it is doomed to failure, e.g. areas of low salinity and low temperatures. It is recommended that potential areas of dispersion be mapped in terms of favorable conditions including salinity and temperature - on a seasonal basis. Further, background information such as plankton concentrations and other points of information should be mapped to ensure that there is a comparison point for future measurements.

4.3 Interaction with Sediment Particles

Studies continued on the formation of oil-mineral aggregates. Once formed oil-mineral aggregates appear to be very stable structures and the buoyancy will depend on the oil to mineral ratio. In studies, it was found that more oil settled to the bottom in the presence of dispersants (Gong, 2014a, b; Khelifa et al., 2011; Wang et al. 2013a, b). Dispersant treatment results in greater numbers of oil droplets and thus greater number of interactions with suspended particulate material (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 there are many findings, notably that oil-SPM particles will often settle to the bottom.

4.4 Dispersed Oil Stability and Resurfacing

The literature confirms the well-known phenomenon that chemically-dispersed oil, as all oil-in-water emulsions, destabilizes after the initial dispersion (Fingas 2011a). The de-stabilization 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 hydrodynamic 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. Data show that for a dilute solution such as a chemically dispersed oil spill, half-lives could vary from 6 to 24 hours, with a typical average value of 12 hours.

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 6 to 24 hours. More study on this is needed and this consideration requires to be incorporated into dispersant effectiveness studies.

4.5 Overall Effects of Weather on Dispersion

Fingas (2011b) 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.

4.6 Sub-surface Application and Subsurface Behavior

The Deepwater Horizon spill was marked by extensive sub-surface use of oil spill dispersants (Nedwed, 2013). It was difficult to separate the effect of the dispersants from other sub-surface release phenomena. There are indeed many behavior and transport processes as a result of a sub-surface release. The most important point is the formation of an underwater plume as a result of what is called a fold-out. The key driving force is the pressure of release which is very high compared to the pressure at the sea floor. As a result of this, there are many chemical changes that occur including solubilization in methane and water (Fingas, 2013). An important fact is that the oil composition as well as the amount of methane is changing as the flow continues. This results in changes to the behavior and composition of the oil dissolving and rising to the surface. This was noted during the Deepwater Horizon spill when some oil rose as emulsion and other times as highly-weathered and un-emulsified oil.

The high velocity jet causes several physical effects, droplet shattering, mixing and water entrainment. Once the velocity has slowed there is a small inversion or fold-out. This is analogous to the mushroom cloud of an explosion. This foldout results in a large amount of water, soluble oil compounds and gases leaving the plume. Scientists noted that this fold out may occur at about 180 meters, dependent, of course, on many conditions such as release pressure. The fold-out itself is an important phenomenon of a blowout. As well, the fold-out gives rise to an underwater plume. This plume is sometimes mistaken for a dispersed oil plume, but it occurs whether or not oil spill dispersant is used and it consists of dissolved material.

The rising plume after a fold-out still has sufficient energy to form water-in-oil emulsions and it may be that they are formed at or above the height of the fold out. In the case of the Macondo Blowout, when the oil hit the water at 81 MPa, it was reduced rapidly to 15 MPa (Fingas, 2013), and the energy was transformed into velocity and the jet region of the plume forms. This jet entrained much water which will be mixed with the oil and dissolved both the gases and some of the oil. At about 180 meters above the blowout entry point, fold-out(s) will occur. These foldouts will discharge water, gases, and oil. These substances will then move off with cross currents. In the water entrained with the plume, there is a large amount of dissolved gas and oil components. These will gradually separate into discrete plumes with some material possibly rising, depending on oceanographic conditions. Once the jet plume phase ends, the velocity of the particles is reduced and the energy has been dissipated with water entrainment and energy transfer to the water column. The remaining oil, after the foldout(s), has undergone massive weathering by loss of volatiles to water dissolution as well as to the gas bubbles which are separating (Fingas, 2013). Because of the rapid pressure reduction, asphaltenes are precipitated into the oil mass and when conditions are right, water-in-oil emulsions are formed. The weathered and sometimes emulsified oil rises slowly to the surface in particle sizes varying from cm to µm sizes. The smaller droplets/particles can take a very long time to rise to the surface.

4.7 Monitoring Application Using Dispersant Components

Dioctyl sulfosuccinate (DOSS) is a major component of the Corexit dispersants and has an aquatic toxicity of approximately double that of the whole dispersant (Mathew et al., 2012). DOSS was found in both waters nearby and distant from areas where dispersant was used.

Mathew et al. (2012) developed a method to quantify DOSS concentrations in sea water to a reporting limit of 20 g/L (20 ppb), which was below the United States Environmental Protection Agency’s 40 µg/L DOSS Aquatic Life Benchmark. It should be noted that DOSS is difficult to sample and analyze in seawater as it partitions to surfaces such as tubes and glassware. Mathew et al. analyzed DOSS in Gulf of Mexico water samples by direct-injection reversed-phase liquid chromatography–tandem mass spectrometry (LC–MS/MS). Sample preparation with 50% acetonitrile enabled quantitative transfer of DOSS and increased DOSS response 20-fold by reducing aggregation. This increased sensitivity enabled the detection over the calibration range of 10–200 g/L. Hundreds of near-shore surface Gulf of Mexico water samples after the dispersant applications during the Deepwater Horizon spill were taken and analyzed. None contained more than the 20 ppb reporting limit.

Ramirez et al. (2013) developed a (LC)–tandem mass spectrometry (MS/MS) method and a direct-injection LC-MS/MS method for the analysis of dioctyl sulfosuccinate in seawater at trace levels, with method detection limits of 7.0 and 440 ng/L and run times of 7 and 17 min, respectively. Stability and preservation studies demonstrated that samples at 4.7 µg/L could be preserved for up to 150 days without loss of analyte when stored with 33 % acetonitrile in glass containers. A modification of the direct-injection method allowed quantitation of 2-butoxyethanol, a dispersant component specific to the Corexit EC9527A formulation. This method was used to simultaneously quantify DOSS and 2-butoxyethanol in two Corexit formulations and extracts from a Deepwater Horizon source oil standard. The method detection limits in crude oil were 0.723 and 4.46 mg/kg, respectively.

Gray et al. (2013) studied DOSS concentrations in the Gulf of Mexico waters after the Deepwater Horizon blowout. Samples of water taken during the blowout at various depths were frozen for six months and then analyzed by LC-MS. The detection level was established as 0.05 µg/L (The EPA reporting level is 40 µg/L). Detections in several water samples were made, always corresponding to those samples that contained hydrocarbons as evidenced by fluorescence. No water samples that did not show oil fluorescence showed DOSS content. Only one sample showed a high DOSS content and that was of 200 µg/L. This sample was taken near the well site and at depth (1200 m).

Several groups studied the use of dipropylene glycol n-butyl ether (DPnB), a solvent component of Corexit dispersants, as a possible marker for the fate and effectiveness of oil dispersion after the Deepwater Horizon spill. There are questions about the partitioning of the marker between oil and water and the fate of the marker. Mudge and others (2011) studied DPnB as it related to the Deepwater Horizon dispersant application. The DPnB present in Corexit EC9500A was found to be a good indicator of the dispersant in the Gulf of Mexico. There was a statistically significant relationship (R^2=0.50, n=27) between the DPnB concentration measured in water samples collected beneath dispersing slicks and the crude oil-derived hydrocarbons. This may provide a measure of the efficacy of the dispersant. The group carried out experiments in open jars which indicated an initial half-life of ~30 days, which is sufficiently long enough to enable samples to be collected after application. There was little contribution of DPnB to the Gulf of Mexico from the Mississippi River at the time of sampling, so it did not confound the measurements made there.

4.8 Human Health Aspects

The Deepwater Horizon spill marked the first time that the effects of dispersants on human health was studied. This was particularly studied through the use of mammal models. Sriram (2011) studied male Sprague-Dawley rats exposed by whole-body inhalation exposure to a model oil dispersant, COREXIT EC9500A (CE; approximately 27 mg/m 3 × 5 h/d × 1 d), and various molecular indices of neural dysfunction were evaluated in discrete brain areas, at 1 or 7 d post exposure. Exposure to CE produced partial loss of olfactory marker protein in the olfactory bulb. CE also reduced tyrosine hydroxylase protein content in the striatum. Further, CE altered the levels of various synaptic and neuronal intermediate filament proteins in specific brain areas. Reactive astrogliosis, as evidenced by increased expression of glial fibrillary acidic protein, was observed in the hippocampus and frontal cortex following exposure to CE. Collectively, these findings are suggestive of disruptions in olfactory signal transduction, axonal function, and synaptic vesicle fusion, events that potentially result in an imbalance in neurotransmitter signaling. Whether such acute molecular aberrations might persist and produce chronic neurological deficits remains to be ascertained.

Roberts et al. (2011) exposed male rats to COREXIT vapor (mean 27 mg/m 3, 5 h). Bronchoalveolar lavage was performed on day 1 and 7 postexposure. Lactate dehydrogenase (LDH) and albumin were measured as indices of lung injury; macrophages, neutrophils, lymphocytes, and eosinophils were quantified to evaluate inflammation; and oxidant production by macrophages and neutrophils was measured. There were no significant effects of COREXIT on LDH, albumin, inflammatory cell levels or oxidant production at either time point. In conscious animals, neither breathing frequency nor specific airway resistance were altered at 1 hr, 1 day and 7 day postexposure. Airway resistance responses to methacholine (MCh) aerosol in anesthetized animals were unaffected at 1 and 7 day postexposure, while dynamic compliance responses were decreased after 1 day but not 7 days. In tracheal strips, in the presence or absence of MCh, low concentrations of COREXIT (0.001% v/v) elicited relaxation; contraction occurred at 0.003-0.1% v/v. In isolated, perfused trachea, intraluminally applied COREXIT produced similar effects but at higher concentrations. COREXIT inhibited neurogenic contractile responses of strips to electrical field stimulation. The findings suggest that COREXIT inhalation did not initiate lung inflammation, but may transiently increase the difficulty of breathing.

Wang et al. (2012) carried out a study designed to examine the cell death and related death pathways of lung epithelial cells in response to WAF. Cultured A549 cells were treated for 2 or 24. h with different concentrations of WAF. The WAF was prepared by mixing each of the dispersants (Corexit EC9527A, Corexit EC9500A and Corexit EC9580A) with crude oil for extraction with PBS. The 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide MTT assay, lactate dehydrogenase assay, morphology and cleaved caspase 9 protein, and microtubule-associated protein were all used to measure cell viability, necrosis, apoptosis and autophagy quantitation, respectively. Results showed that the WAF of oil-dispersant mixtures caused cell death in the lung epithelial cells, in a dose-dependent manner, with the major cellular pathways of necrosis and apoptosis involved. Autophagy also occurred in cells exposed to WAF mixtures at lower concentrations before any detectable cell death, indicating greater sensitivity to WAF exposure. The three types of cell behavior, namely necrosis, apoptosis and autophagy, may play different roles in oil spill-related respiratory disorders.

Cerniglia et al (2012) carried out studies to examine the cell death and related death pathways of lung epithelial cells in response to WAF. Cultured A549 cells were treated for 2 or 24. h with different concentrations of WAF. The WAF was prepared by mixing each of the dispersants (Corexit EC9527A, Corexit EC9500A and Corexit EC9580A) with crude oil for extraction with PBS. The 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide MTT assay, lactate dehydrogenase assay, morphology and cleaved caspase protein, and microtubule-associated protein 1were all used to measure cell viability, necrosis, apoptosis and autophagy quantitation, respectively. Results showed that the WAF of oil-dispersant mixtures caused cell death in the lung epithelial cells, in a dose-dependent manner, with the major cellular pathways of necrosis and apoptosis involved. Autophagy also occurred in cells exposed to WAF mixtures at lower concentrations before any detectable cell death, indicating greater sensitivity to WAF exposure. The three types of cell behavior, namely necrosis, apoptosis and autophagy, may play different roles in oil spill-related respiratory disorders, similar to that noted by Wang et al., (2012).

D'Andrea and Reddy (2013) studied the adverse health effects of the Gulf oil spill exposure in subjects participating in the clean-up activity along the coast of Louisiana. This retrospective study included subjects that had been exposed and unexposed to the oil spill and dispersant. Using medical charts, clinical data including white blood cell count, platelets count, hemoglobin, hematocrit, blood urea nitrogen, creatinine, alkaline phosphatase (ALP), aspartate amino transferase (AST), alanine amino transferase (ALT), and somatic symptom complaints by the subjects were reviewed and analyzed. Results A total of 247 subjects (oil spill exposed, n = 117 and unexposed, n = 130) were included. Hematologic analysis showed that platelet counts (× 103 per μL) were significantly decreased in the exposed group compared with those in the group unexposed to the oil spill (252.1 ± 51.8 vs 269.6 ± 77.3, P =.024). Conversely, the hemoglobin (g per dL) and hematocrit (%) levels were significantly increased among oil spill-exposed subjects compared with the unexposed subjects (P =.000). Similarly, oil spill-exposed subjects had significantly higher levels of ALP (76.3 ± 21.3 vs 61.2 ± 26.9 IU/L, P =.000), AST (31.0 ± 26.3 vs 22.8 ± 11.8 IU/L, P =.004), and ALT (34.8 ± 26.6 vs 29.8 ± 27 IU/L, P =.054) compared with the unexposed subjects. The results of this study indicate that clean-up workers exposed to the oil spill and dispersant experienced significantly altered blood profiles, liver enzymes, and somatic symptoms

Krajnak et al., 2011 studied cardiovascular responses after an acute inhalation exposure to COREXIT EC9500A, the oil dispersant used in the Deepwater Horizon oil spill. Male Sprague-Dawley rats underwent a single 5-h inhalation exposure to COREXIT EC9500A (average exposure level 27.12 mg/m^3) or air. On d 1 and 7 following the exposure, rats were implanted with indwelling catheters and changes in heart rate and blood pressure were assessed in response to increasing levels of adrenoreceptor agonists. A separate group of rats was euthanized at the same time points, ventral tail arteries were dissected, and vascular tone along with dose-dependent responses to vasoconstricting and dilating factors were assessed in vitro. Agonist-induced dose-dependent increases in heart rate and blood pressure were greater in COREXIT EC9500A-exposed than in air-exposed rats at 1 d but not 7 d after the exposure. COREXIT EC9500A exposure also induced a rise in basal tone and reduced responsiveness of tail arteries to acetylcholine-induced vasodilation at 1 d but not 7 d following the exposure. These findings demonstrate that an acute exposure to COREXIT EC9500A exerts transient effects on cardiovascular and peripheral vascular functions..

In summary, tests of inhalation models showed that there might be a concern over human inhalation of dispersant vapors, however the exposures and the levels of exposures may not be pertinent to at sea applications. Further study certainly is needed.

5 Recommendations for Further Research

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 literature 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, whenever 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.

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