A Review of Literature Related to Oil Spill Dispersants

for

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by

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Abstract

This report is a review of the literature on oil spill dispersants published through May 2017. The report identifies and focusses on recent advances in all topics of dispersion and focusses on dispersant effectiveness, toxicity, and biodegradation.

There are three ‘issue pillars’ for dispersants: effectiveness, toxicity and biodegradation. Effectiveness includes the focus that dispersants must be highly effective to meet the stated objectives of protecting wildlife on the water surface and keeping oil from the shoreline. Secondly, the toxicity of the dispersed oil and the dispersant itself must not lead to environmental damage above and beyond that of undispersed oil. Finally, the biodegradation of oil should be aided and not hindered by the application of dispersants.

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. Ideally, oil should not come ashore if dispersants are used. Nor should birds and other biota be oiled if dispersants were highly effective.

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 alone is typically less than the toxicity of dispersed oil. Of the recent toxicity studies of dispersed oil, most 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 found that the toxicity of chemically-dispersed oil was equivalent to physically-dispersed oil.

The effect of dispersants on biodegradation is still a matter of dispute, however all but one study in the current series, showed dispersants inhibit biodegradation. The reason for this appears to be selective toxicity of some dispersant ingredients to certain oil-degrading microorganisms. This selective toxicity results in a population shift which changes the types and rates of hydrocarbons degraded, with the frequent overall result that biodegradation is slowed compared to that of situations where dispersant was not used.

Several important sub-topics are included in this review. The formation of marine snow, a natural aggregate which sinks to the bottom with oil droplets, is enhanced by the presence of dispersants. The interaction of oil droplets, particularly chemically-dispersed droplets, with mineral particles appears to be an important facet of oil fate. Several other facets of dispersants are summarized in this review.

Executive Summary
Effectiveness

In recent times, effectiveness studies have not been pursued as intensely as before. Work in the area is very low compared to the three previous reviews. There are only a few studies on effectiveness.

One of the major confusions that persist is the relationship of effectiveness to viscosity. There is a certain belief that a ‘viscosity cut-off’ 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. Strictly speaking, a ‘viscosity cut-off’ does not exist as a global value.

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. Laboratory tests are quite useful in studying chemical and physical parameters of dispersion on controlled conditions. Currently, the only extensive work is being carried out in laboratories.

Laboratory Testing

Some laboratory testing was carried out in this time period, less than in previous literature review time periods. Physical studies were largely carried out in the swirling flask test, that is known for high repeatability and ability to discriminate widely between differing conditions, dispersants and oils. Some effectiveness studies have been carried out in the baffled flask, that test is known to yield higher effectiveness values due to its higher energy. The differences between the two tests revolve around the fact that the baffled flask has a much higher turbulent energy than the swirling flask. The difference is sometimes exaggerated by some authors who used non-standard analytical means such as colorimetry or spectrophotometric means. These methods are known to produce high and variable results compared to the standard chromatographic methods. During this time period, ASTM released a new standard using standard chromatographic analysis for the baffled flask. A similar standard for the swirling flask has been extant for about 20 years.

In addition, there are several points that can be made about laboratory effectiveness testing:

- There have not been strong attempts to relate effectiveness results to at-sea results in any of the studies in this or the last literature reviews; however; previous comparisons to at-sea tests showed the swirling flask was much closer than others, albeit it still showed too high effectiveness. The other tests yield far too high effectiveness values.

- The purpose of laboratory testing was and still is, to screen oil and dispersant combinations for effectiveness and to conduct specific physical studies.
- Laboratory tests show that viscous oils are largely not dispersible.
- The dispersibility in the swirling flask can be correlated to physical and chemical properties of oils.
- The rising time in laboratory tests is a critical component, studies show that at least 20 minutes is required to provide a stable sampling time. This rising time and the results of variable sampling times show the relative instability of dispersions with time.
- The effect of dispersant ingredients should be examined further, one study showed that there were concerns with effectiveness and droplet size with differing combinations of dispersant ingredients.
- There were no new testing results for ANS.

Tank Tests

While tank tests continued during the time period of this review, there was not a full consideration of the testing factors noted in previous reviews. There are several findings that might be noted:

- Dilbit or diluted bitumen is only dispersible when fresh, there is some disagreement about the degree of weathering before the product becomes less dispersible.
- Salinity is an important factor in oil dispersibility; dispersibility decreases with decreasing salinity.
- Paraffinic crudes are less dispersible.
- As weathering increases for crude oils, dispersants become increasingly ineffective.
- As weathering increases for Dilbits, shoreline cleaners also become ineffective.

Analytical Techniques for Effectiveness

Analytical techniques as applied to dispersant effectiveness are a major issue. It should be noted that only ASTM or EPA standard chromatographic methods are considered valid for the measurement of oil in water. No spectrophotometric or fluorimetric methods will yield reliable quantitative results. These optical methods yield near-random and high results. There are standard ASTM methods of analysis and measurement of laboratory effectiveness. There are no simple ways to measure dispersant alone in water; however, there are sophisticated methods.

General Analytical Techniques

Major steps have been made in recent years in the analysis of dispersant components, especially for DOSS or bis-(2-ethylhexyl) sulfosuccinate, which is a major component of Corexit dispersants. Further, this component can now be measured in water or environmental samples such as bird eggs, down to parts per billion quantities, allowing for several important environmental fate studies. Methods have also been developed for other dispersant components such as the Tweens, Spans and solvents; however, the sensitivity is not as great. Studies in the case of the Deepwater Horizon have been able to track DOSS over dozens to hundreds of kilometers, however not so for the Tweens, Spans and solvents, leading to speculation on the fate of these particular components.

Studies on the asphaltene component of the Macondo oil enable one group of researchers to calculate that the weathering of the oil on the surface had progressed as far as a loss of 61% including that lost by dissolution in the subsurface. Others used analytical techniques to improve mass balance calculations during the DWH incident.

Specialized analytical techniques have been applied to the study of surfactants themselves and their critical micelle concentration.

Several studies have made on the effect of dispersant content on oil fingerprinting and analysis. Findings are that there are differences caused by dispersants, however higher-molecular weight biomarkers do not appear to be affected.

Toxicity to Biota

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. 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 and the large increase in PAHs in the water column as a result of dispersant use.

Aquatic Toxicity of Dispersants with Oil

Toxicity studies in the period of 2014 to 2017 involved more than 220 individual studies conducted by more than 25 separate study groups. 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 and subsequent funding. The overall summary result of these tests is that 6% of the studies where such comparison could be made, found that chemically-dispersed oil was less toxic than mechanically-dispersed oil. Seventeen percent (17%) of the studies where comparison could be made, noted that the chemically- and mechanically-dispersed oil had about the same toxicity. Seventy-eight (78%) percent of the studies noted that chemically-dispersed oil was more toxic than mechanically-dispersed oil. If the latter is divided into two categories, 45% showed that chemically-dispersed oil was somewhat more toxic than mechanically-dispersed oil; whereas, 33% showed that chemically-dispersed oil was much more toxic than mechanically-dispersed oil.

The many toxicity studies of water-accommodated fractions (WAF) versus chemically-enhanced water-accommodated fractions (CEWAF) show the following generalizations:

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, which may be specific to a study or if more general, these generalizations will be captured in this review.

c) For a few 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 most studies, it was found that CEWAF was from slightly to 1.5 to 100 to as much as 500 times more toxic than the WAF, depending on the variables.
e) Some studies showed that the CEWAF toxicity was as a result of the increase of PAHs compared to WAF which puts less PAHs, into the water. The PAHs sometimes corresponded to the toxicity increase shown in d) 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.
h) The question of why some chemically-dispersed oil appears to be more toxic than mechanically-dispersed oil may relate to the increased amounts of PAHs in the water with chemical dispersions. This is especially true of the aquatically-toxic 2-ring and 3-ring PAHs.
i) Some workers have suggested that CEWAF is more bioavailable than mechanically-dispersed oil. This is in addition to the note in h).
j) Photo-susceptible species are particularly vulnerable to increased water concentrations of PAHs caused by chemical dispersion.
k) Juvenile forms of most species are much more susceptible to both CEWAF and WAF.
l) Although weathered oil is generally shown to be less toxic to species (chemically- or mechanically-dispersed), calculation of its PAHs may make it appear as though it is as toxic or more toxic than un-weathered oil. It is suggested here, that irrespective of some apparently-incorrect calculations, that weathered oil is always less aquatically-toxic than its un-weathered counterparts.
m) Some species are more susceptible to oil droplets than others, thus these species are more prone to chemically-dispersed oil than those species which are not susceptible to oil droplets.
n) Generalizations about dispersants should not be made if the dispersant itself is different from those in other studies. Many studies used Corexit 9500, however, other studies did not use Corexit and in some cases used relatively unknown and unstudied dispersants.

General Effects on Biota and Wildlife

Several studies **o**n wildlife and other biota were carried out in this review time period. Studies in this time period showed similar results to previous studies that corals are very sensitive to oil and particularly dispersants and dispersed oil. This is caused by the fact that the external membrane of the coral is permeable to oil components and dispersants. Studies in the past two decades have repeated these findings. This should be cause to re-examine the use of dispersants in any area where the dispersed oil or dispersant can be carried to corals.

Other effects on various wildlife include:

- Several studies of the aftermath of the Deepwater Horizon spill show that deep-sea corals were damaged up to 14 km away from the drill site. This damage was largely caused by suffocation from oil mats and flocculent layers of oil.
- Some fish larvae are affected by dispersed oil, however others, such as mackerel larvae are not as sensitive.

- Turtles may be susceptible to oil and dispersants, however, tests have yet to be developed to show this.
- Marsh impacts by oil and dispersed oil were severe during the DWH spill, however the specific impacts of the dispersant are unknown.
- Birds eyes are affected by oil and more so by dispersants.
- Dolphins show genetic response to dispersed oil, however as in turtles, more testing is required.
- Mangroves may also show response to dispersed oil, however, further work is also necessary.

Photo-enhanced Toxicity

Certain biota have transparent life phases and spend portions of their life near or on the sea surface. Some of these biota are prone to photo-enhanced toxicity. Photo-enhanced toxicity consists of two mechanisms, but the most important one is photosensitization. This occurs when a PAH absorbs energy from the light and then transfers this to dissolved oxygen. This results in enhanced toxicity to many organisms. The tests of photo-enhanced toxicity show that oil and especially dispersed oil is increased by UV light. Increases of 1.5 to 4 for noted for physically-dispersed oil and from about 4 to 48 times for chemically-dispersed oil. This photo-enhanced toxicity is particularly applicable to dispersant application in shallow waters.

Testing Protocols

CROSERF aquatic testing protocols have been around for more than two decades and were developed in an era of lesser analytical capability. These protocols have never been fully characterized in terms of modern analytical standards. It is suggested that the protocols be re-evaluated with the current analytical and droplet size measurement capabilities.

Biodegradation

Overall, one might note that many of the experimental systems used to investigate biodegradation might be inappropriate to represent the environment, because they apply high mixing energy in an enclosed, nutrient-sufficient environment and allow 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. Only PAH mineralization (that is complete degradation to CO_2) can be equated with toxicity reduction. Stimulation of alkane biodegradation is not meaningful in the overall fate 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. 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 would not count these polar compounds 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. Therefore, conventional techniques may overstate biodegradation by as much as four times.

This present review found that most authors conclude that most studies found that dispersants suppress biodegradation. This present study rated 11% of the reviewed papers as showing neutral results; 22 % as showing positive results (notably - all industry funded) and 67% of the rated studies as showing suppression of biodegradation by the presence of dispersants. These results are consistent with past reviews.

In addition, the following points are noted:

- When components of dispersants were tested separately, often these components had differing effects on the inhibition or promotion of biodegradation.
- Toxicity to some species of microbial biodegraders may be a factor that causes these varying results.
- There is a species shift with dispersants involved, as will be shown in the next section.
- Deep sea biodegradation may involve different dynamics than surface biodegradation and may require separate tools to investigate this phenomenon further.

Bacterial Population Shifts

Several studies have shown that the presence of dispersants alters both the numbers and succession of hydrocarbon degrading organisms. This appears to be the result of selective toxicity of dispersants to some species while other species are tolerant of dispersants. This effect is different for different dispersants and different dispersant constituents. The end result of this number and succession shift is generally a reduction in biodegradation compared to a situation where dispersants are not used.

Marine Snow Formation

Marine snow (formation of mucous-like agglomerates including oil) production occurs during spills and is increased by the presence of dispersants. Marine snow results in the sedimentation of oil to the sea floor, where its fate is relatively unknown. Studies of past spills show that these spills precipitated increased amounts of marine snow. Studies of the Deepwater Horizon spill shows that as much as 14% of all the oil may have been sedimented to the sea floor as marine snow.

Fate Impacted by Dispersant Use

The studies dealing with the oil fate as impacted by dispersants, show that dispersants do increase the amount of BTEX into the water column, as is already known. Further, one study shows that dispersions also change the processes of fecal pellets in copepods by incorporating smaller oil droplets.

Other Topics

Dispersant Use in Recent Times and NEBA

Much of the discussion still revolves around the use of dispersants during the Deepwater Horizon spill. Re-evaluation of this spill should consider the fact that neither sub-sea nor on-sea dispersion was evaluated in detail for effectiveness. Discussion will continue on how effective these applications really were. This is especially true considering the large amounts of oil observed to have impacted the shoreline and to have sedimented to the seafloor.

Focus on dispersant use continues on using NEBA or Net Environmental Benefit Analysis and good communication with stakeholders.

Monitoring Dispersant Effectiveness

New dispersant effectiveness monitoring protocols have been suggested and published. These include the following advances: use of a field effectiveness test to pre-screen slicks for effectiveness; new guidelines for visual observation of effectiveness along with required times; use of modern instruments that measure particle size and with the ability to integrate these into total oil measurements; sampling and analysis of water below slicks; and shipboard toxicity measurements.

Interaction with Sediment Particles

Several studies continued on oil-sediment interaction. Results are conclusive that dispersants increase the amount of oil-sediment aggregates formed as a result of the more droplets of oil in the water column at the time of formation. Increasing the sediment content in a dispersion, also increases the total amount dispersed. The mineral aggregates thus formed will sediment to the sea bottom, given time and quiescence. There are variabilities in these processes with temperature, oil type, oil viscosity and oil weathering.

Dispersed Oil Stability and Resurfacing

Consideration of water-in-oil dispersion stability is an important matter. It is known that oil spill dispersions are sometimes temporary and re-surfaced slicks can appear. Further the amount of oil entering the water has been shown to be highly variable and this has also been observed to be related to the oil properties and the sea energy. An important facet of the problem is the slow rise and coalescence of droplets to the surface after dispersion. 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. 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.

Sub-surface Application and Subsurface Behavior

Studies on the results of deep-sea injection of dispersants, especially the effect on droplet size, have not used directly-scalable simulative studies. Modeling or scale studies remain as the only means to address the questions. The results vary and to date there has been no definitive answer if the injection of dispersants during the Deepwater Horizon reduced droplet size or had any other effect.

Human Health Aspects

Several studies of different types were applied. Many of the results could be considered preliminary since they were one-off studies and many indicated marginal results.

Application of several standard procedures indicated that:

- The health risk to children from touching beach sand that had been contaminated by oil and/or dispersant was low.
- The health risk from approved sea food was low and maybe less than the risk from inland sea food.
- There was low risk to cleanup workers of exposure to inhalation of high levels of toxicants however blood levels of some oil constituents were found in workers.
- There was lung epithelial tissue toxicity from Corexit dispersants.
- Corexit was found to be somewhat cytotoxic.
- It was found that there were stress symptoms such as depression and anxiety among cleanup workers as well as their families, with no particular relation to the use of dispersants.
- DOSS, an ingredient of Corexit, was found to be an obesogen; however, one would need to ingest DOSS to cause this effect.

Effects on Photooxidation and Photodegradation

Limited studies have been carried out showing that dispersants enhance the photodegradation of PAHs resulting in increased toxicity of the oil and dispersant under the influence of sun.

Modeling

Modeling is becoming an increasing activity and source of information in addition to the traditional provision of predictions. In this review, almost every conceivable facet of oil spill and oil spill fate and behavior was modeled. If modeling results are accurate, these data are very useful. Some of the studies have involved obtaining data, typically from laboratory model systems, to develop the modeling algorithms. There are many types of models summarized in this review. The following points can be made:

- Many 3-dimentional oil spill models are published, whereas before, most were 2-dimentional. This 3-D capability enables the calculation of dispersion.
- More models now include a variety of facets including movement, impact, fate and effects.
- An important field of modeling is the understanding of processes. In this time period, there is much focus on understanding the production of oil droplets and their sizes and size ranges.
- Extensive effort was placed on studying the dynamics of the Deepwater Horizon spill, especially that of the sub-sea discharge.
- There are now chemical dispersion models with some empirical basis, albeit rather old inputs.
- There exists a strong need for more actual data at full scale to calibrate and develop models.
- Over-reliance on models to understand natural systems, can occur in the absence of actual data.

New Dispersants

In this review, approximately 30 ideas on new products are summarized. Most of these products are often based on natural products such as chitosan, xanthum or lecithin. Most of these products were not tested in a standard way and most were never developed further than a laboratory idea and a subsequent paper.

Surface Application

Aerial application is largely the current application method; whereas, ship application work has largely been sidelined. Some new application packages have been developed in recent years and others improved.

Fate of Dispersants

Several studies on the fate of dispersants and how they influence the fate of oil, have been carried out. Findings include:

- Dioctyl sulfosuccinate (DOSS) and dipropylene glycol butyl ether (DGBE), two ingredients of Corexit 9500, may be subject to photolysis and photodegrade in near-surface waters.
- The dispersant Corexit 9500 appears to inhibit the photodegradation of PAHs.
- Span 80, a surfactant ingredient in Corexit 9500, may increase the aerosolization of oil.
- Dispersants increase the sediment uptake of PAHs.

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 Nalco
Corexit 9500 - Brand name of a dispersant from Nalco
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 (alternatively DeepWater Horizon), also known as the Macondo spill
Intersperse - 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 - egg. IFO 180 and 380 refer to the viscosity of the oil at about 38ºC
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

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1 Introduction

1.1 Objectives

The objectives of this review are to summarize the literature from 1999, including summary information from the last reports, to the current date (2017) 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 2014 the last review, including literature from 1999. As such it covers all known dispersant-related literature from that time period to May of 2017. Summary information from the previous reports (2002, 2008 and 2014 has also been included).

1.3 Organization

The report begins with a summary and then provides a detailed review of the literature. Where relevant each section and sub-section has four sub-headings; Introduction Summary and Conclusions, Detailed Study Summaries, and Results from Previous Literature Reviews. This enables the reader to focus on summaries if they do not wish to read all the details or to focus on specific topics.

A review of the overall dispersant situation is presented in Section 2. In Section 3, the major topics of effectiveness, toxicity and biodegradation, are discussed. In Section 4, other topics, particularly those relevant to PWSRCAC, are summarized as drawn from the literature review. Section 5 presents recommendations.

2 Overview of Dispersants

The use of dispersants still generates debate five decades after the 1967 Torrey Canyon incident. Some of the same issues predominate. 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 50 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. 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*" (Fingas, 2014).

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, but generally biodegradation is suppressed. 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 many oil-degrading bacteria, are more predominant near 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 Topics

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 (Fingas, 2014). 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 dispersant effects on real spills 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 (Fingas, 2014). 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 number 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 therefore remain largely as a topic for speculation. On a community level, there have been very few studies (Fingas, 2014), moreover no molecular-level studies were undertaken in any of these studies.

3 Review of Major Dispersant Topics

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

Introduction

In recent times, effectiveness has not been an important issue. Work in the area is very low compared to the three previous reviews. While there are a variety of reasons for this low research activity, there are nevertheless, studies on 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, perhaps hours or days) 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 cut-off' 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. Strictly speaking, 'viscosity cut-off', as a global term, 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 few 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 (Fingas, 2014). 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 was 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 affect the outcome in one direction, and as well as 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 (Fingas, 2014). 0ften, oil spill personnel ignore the matter of effectiveness and discuss the benefits of their use, which are entirely based on complete effectiveness (Prince, 2015; Prince et al., 2016).

3.1.1 Field Trials

Introduction and Summary

In the last review period, 2014 to 2017, no field trials were carried out, however, data from older field trials are often cited. Some of these field trials were flawed in the sense that incorrect procedures or analytical procedures were used. Further, some of the results were not placed into the context of the dispersant used, the oil used or the sea energy available.

The U.S. National Academy of Sciences noted several items about field trials (Fingas, 2014). 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 aromatic composition, and therefore with time. 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.

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, 2014 and references therein). 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 thirty years, offshore trials have been conducted in the North Sea primarily by Great Britain and Norway (Fingas, 2014). 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. Later 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. The validity of older test results is even more questionable because of both the analytical methodology and data treatment methods (Fingas, 2014). It is interesting that the percentage values assigned to all field tests ever conducted, average 19%.

Most tests relied heavily on developing a mass balance between oil in the water column and that oil left on the surface (Goodman, 2014). 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 for the last 25 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.

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 amounts of hydrocarbons in the water column was greatly exaggerated. Since the colorimetric techniques used at the time always yielded some value of hydrocarbons and never zero, the effectiveness values were significantly inflated. 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, 2014).

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.

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., 2014).

3.1.2 Laboratory Tests

Introduction

Many different types of procedures and apparatus for testing dispersants are described in the literature. Fifty different tests or procedures are described in the past (Fingas, 2014). Only a handful of these are commonly used, however, including the or rotating flask test (also known as the Warren Springs test, the swirling flask test, and the baffled flask test. About 20 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 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, 2014).

Summary and Conclusions

Some laboratory testing was carried out in this time period, less than in previous literature review time periods. Physical studies were largely carried out in the swirling flask test, that is known for high repeatability and ability to discriminate widely between differing conditions, dispersants and oils. Some effectiveness studies have been carried out in the baffled flask, that test is known to yield higher values due to its higher energy. The differences between the two tests revolve around the fact that the baffled flask has a much higher energy than the swirling flask. The difference is sometimes exaggerated by some authors who used non-standard analytical means such as colorimetry or spectrophotometric means. These methods are known to produce high and variable results compared to the standard chromatographic methods. During this time period, ASTM released a new standard using standard chromatographic analysis for the baffled flask. An ASTM standard for the swirling flask has been extant for about 20 years.

In addition, there are several points that can be made about laboratory effectiveness testing:

- There have not been strong attempts to relate effectiveness results to at-sea results in any of the studies in this or the last literature reviews; however; previous comparisons to at-sea tests showed the swirling flask was much closer than others, albeit it still showed too high effectiveness. Other tests showed too high values - up to 10 times that of the at-sea measurement.

- The purpose of laboratory testing was and still is to screen oil and dispersant combinations for effectiveness and to conduct specific physical studies
- Laboratory tests show that viscous oils are largely not dispersible
- The dispersibility in the swirling flask can be correlated to physical and chemical properties of oils
- The rising time in laboratory tests is a critical component, the studies show that at least 20 minutes is required to provide a stable sampling time. This fact and the results of variable sampling time show the relative instability of dispersions with time
- The effect of dispersant ingredients should be examined further, one study showed that there were concerns with effectiveness and droplet size with differing combinations of dispersant ingredients.
- There were no new testing results for ANS.

Detailed Study Summaries

ASTM released a new standard (2017) for the baffled flask which uses standard chromatography for the analytical method. This accompanies the long-standing and recently-updated swirling flask standard.

Bess and Young (2016) present several alternate methods to predict oil dispersibility in the US EPA swirling flask test using Corexit 9500 as well as a comparison with data for several other dispersants in the same test. The oil properties chosen can result in acceptable dispersibility prediction.

Fieldhouse et al. (2014) weathered 2 diluted bitumen products using rotary evaporator to prepare samples at four weathering states between fresh, to highly weathered residue. The effectiveness of the dispersant Corexit EC9500A was determined for each of the samples by both the low-energy Swirling Flask Test (SFT) and the high-energy Baffled Flask Test (BFT) at temperatures ranging from 5 to 25 °C. The results showed that dispersants were ineffective on oil sands products at all temperatures in the SFT. while the BFT had a somewhat more positive result. The BFT results were correlated to the rheologic properties of the samples to establish a limiting threshold value corresponding to a stable dispersion. Pan evaporation experiments were conducted for one week to estimate the exposure time required to reach the weathered states relevant temperatures. A plot of the rheologic properties against exposure time provided an estimate of the time window-of-opportunity for effective dispersant use at environmental temperatures. The rapid depletion of volatile components to leave a heavy residue generally limited the effective use of dispersants on diluted bitumen to less than 12 hours at temperatures below 15 °C, even when measured at the high energies in the BFT.

Fieldhouse et al. (2016) evaluated five classes of spill countermeasure on a range of oil sands products and reference oils using standard test methods. Dispersant testing indicates that effectiveness is limited by viscosity; the high proportion of interfacially active asphaltenes and resins in some oil sands products reduce dispersibility, especially as weathering occurs. Surface washing agent tests indicate that effectiveness is reduced for highly-weathered dilbit residues relative to the other oil sands and reference oils, attributable to the lower mobility of the bituminous residue compared to other oils that contain a higher proportion of mid-range hydrocarbons. Results from herder testing suggest that slicks of fresh oil sands products contract similarly to other oils, with the slick thickness governed primarily by the viscosity of the oil. Solidifier testing shows only a small variance due to the oil type, with performance tied primarily to the solidifier agent.

Pan et al. (2017) studied effects of mixing time and energy on Alaska Northern Slope (ANS) and diluted bitumen Cold Lake Blend (CLB) were investigated using EPA baffled flask test, with the non-standard analytical method using colorimetry. Dispersion effectiveness and droplet size distribution were measured after 5–120 min. A modeling method to predict the mean droplet size was introduced to elucidate the droplet size breakup mechanism. Droplet measurement techniques were not detailed. The ANS dispersion effectiveness greatly increased with dispersant and mixing energy. However, little CLB dispersion was noted at small energy input. With dispersant, the ANS droplet size distribution reached quasi-equilibrium within 10 min, but that of CLB seems to reach quasi-equilibrium after 120 min. Dispersants are assumed ineffective on high viscosity oils because dispersants do not penetrate them. The authors provide an alternative explanation based on the elongation time of the droplets and its residence in high intensity zones. When mixing energy is small, CLB did not disperse after 120 min, long enough to allow the surfactant penetration.

Riehm and McCormick (2014) measured dispersion effectiveness of dispersants containing Tween 80, Span 80, and dioctyl sodium sulfosuccinate (DOSS) using a modified Swirling Flask test, and was correlated with both initial and dynamic interfacial tension produced by those dispersants at an oil-water interface. Compositional trends in effectiveness were shown to be governed by: (1) initial oil-water interfacial tension observed upon dispersant-oil-saltwater contact; (2) rate of increase (or decrease) from the initial interfacial tension as DOSS was rapidly lost to the aqueous phase; and (3) gradually slowing kinetics of dispersant adsorption to the oil-water interface as Span 80 concentration was increased, which ultimately diminished dispersion effectiveness considerably even as dynamic interfacial tension remained $<10^{-3}$mN/m. It is proposed that this third phenomenon results not only from the hydrophobicity of Span 80, but also from the dependence of mixed Tween-Span-DOSS reverse micelles' stability in crude oil on dispersant composition

Riehm et al. (2016) studied DOSS (dioctyl sodium sulfosuccinate), Tween 80, and Span 80, surfactants used in dispersants, and mixed these into a model oil at a total surfactant concentration of 2 wt % (1:50). These surfactant-oil blends also contained 0.5-1.5 wt % synthetic seawater to enable formation of water-in-oil microstructures. Trends in dynamic oil-seawater interfacial tension as a function of surfactant blend composition are similar to those observed in prior work for crude oil treated with similar blends of these surfactants. In particular, Span 80-rich surfactant blends exhibited much slower initial dynamic IFT decline than DOSS-rich surfactant blends in both model oil and crude oil, and surfactant blends containing 50 wt % Tween 80 and a DOSS:Span 80 ratio near 1:1 produced ultralow IFT in the model oil ($<10^{-4}$ mN/m) just as similar surfactant blends do in crude oil. At all DOSS:Span 80 ratios, surfactant blends containing 50 wt % Tween 80 form clear solutions with seawater in the model oil. Cryo-transmission electron microscopy and dynamic light scattering show that these solutions contain spherical W/O microstructures, the size and dispersity of which vary with surfactant blend composition and surfactant:seawater molar ratio. Span 80-rich microstructures exhibit high polydispersity index and large diameters (≥100 nm), whereas DOSS-rich microstructures exhibit smaller diameters (20-40 nm) and low polydispersity index, indicating a narrow microstructure size distribution. The smaller diameters of DOSS-rich microstructures, as well as the fact that DOSS molecules, being oil-soluble, can diffuse to a bulk oil-water interface as monomers much faster than any of these microstructures, may explain why DOSS-rich blends adsorb to the oil-water interface more quickly than Span 80-rich blends, a phenomenon which has been linked in prior work to the higher effectiveness of DOSS-rich Tween/Span/DOSS-based oil dispersants.

Salnikov and Gribov (2015) propose a new fast method of determination of effectiveness of dispersants for the Arctic seas. The method is purported to be simple and doesn't demand expensive equipment and highly skilled personnel, and also allows several parallel experiments. Details of this are, however, not available.

Sun et al. (2016) conducted a laboratory study to investigate the effectiveness of a widely used chemical dispersant in China under different mixing conditions, aiming to determine the optimum condition to apply this dispersant. TOPO crude oil and diesel oil were selected as the test oil. Filtered natural seawater, baffled flasks and a reciprocating shaker were used for the controlled experiment. The roles of oil type, and different environmental factors like mixing time, salinity and temperature in dispersant efficiency were studied systematically. The dispersant efficiency was evaluated based a settling time of 30 s and 10 min, respectively. The dispersed oil in the aqueous phase was characterized using an ultraviolet spectrophotometer. The results showed that oil type, the mixing energy applied, and temperature were key factors influencing the effectiveness of the dispersant. The highest effectiveness with a settling time of 30 s was 91%, and 65% with a settling time of 10 min. The dispersant efficiency increased with increase of the duration of the mixing energy applied, and also with the increase of temperature of the seawater from 10 to 30 °C.

Zhao et al. (2016b) investigated the mixing energy in the baffled flask. Particle image velocimetry (PIV) was used to measure the water velocity and energy in the flask placed at an orbital shaker that was rotated at seven rotation speeds: 100, 125, 150, 160, 170, 200, and 250 rpm. Two-dimensional velocity fields in large and small vertical cross sections of the flask were obtained. The one-dimensional energy spectra indicate the existence of inertial subrange. The estimated average energy dissipation rates were in the range 7.65×10^{-3} to 4 W/kg for rotation speeds of ω=100-250 rpm, of which it is larger than the one estimated by prior studies using single-point velocity measurement techniques for ω=100 and 200 rpm. Factors such as instruments used, velocity components measured, and different analysis methods could contribute to such discrepancies. The Kolmogorov scale estimated in this study for all seven rotation speeds approached the size of oil droplets observed at sea, which is 50-400 µm. The average energy dissipation rate, e and Kolmogorov microscale, n, in the flasks were correlated to the rotation speed, and it was found that $\bar{e}=9.0\times10^{-5}\exp(0.043\omega)$ with R^2=0.97 and $\bar{n}$=1,463 Exp(-0.015ω) with R^2=0.98.

Results from Previous Literature Reviews

2002 The efficacy of dispersants in Alaskan waters remains an unknown. Recent literature shows that the effectiveness of Corexit 9527 on Alaska North Slope, as measured in laboratory tests at the same temperatures and salinities as found in Prince William Sound, would range from 5 to

10%. Tests at regular temperatures for range show effectiveness for Corexit 9527 range from 16 to 57% for Prudhoe Bay or Alaska North Slope crude oils. High-energy tests show percentages above this mark. Some new data questions the high-energy test results, indicating that in the field, results even lower than the moderate-energy tests are more likely.

2008 Effectiveness remains a major issue with oil spill dispersants. It is important to recognize that many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water. The most important of these is the composition of the oil, followed closely by sea energy and the amount of dispersant applied. It is equally important to recognize that the only thing that matters in the end is effectiveness on real spills at sea. More emphasis might be put on monitoring this so the world has the real information for assessment and modeling.

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

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

2014 Effectiveness is still an 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 shows major deficiencies. Emphasis should be on real results from real spills.

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.

3.1.3 Tank Tests

Introduction

There were some tank tests for effectiveness during this literature review period. The last U.S. National Academy review focussed much attention on tank testing (Fingas, 2014). 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 values associated with the non-dispersion parameters of mass balance can be mistaken for dispersion if mass balance is not calculated.

Summary and Conclusions

While tank tests continued during the time period of this review, there was not a full consideration of the testing factors noted in the introduction above. There are several findings that might be noted:

- Dilbit or diluted bitumen is only dispersible when fresh, there is some disagreement about the degree of weathering before the product becomes less dispersible.
- Salinity is an important factor in oil dispersibility, dispersibility decrease with decreasing salinity.
- Paraffinic crudes are less dispersible.
- As weathering increases for many crude oils, dispersants become increasingly ineffective.
- As weathering increases for Dilbits, shoreline cleaners also become ineffective.

Detailed Study Summaries

Several dispersant effectiveness tests using the SL Ross meso-scale tank on four Alaskan crude oils with four water salinities were conducted to examine the effectiveness of a marine dispersant over a range of water salinities under high energy breaking wave conditions (Belore, 2015). Alaska North Slope, Endicott, Northstar and Kuparuk crude oil were used in the testing. Tests were conducted on fresh, evaporated and evaporated plus emulsified crude oils. Tests were conducted in water with salinities of 5, 10, 20 and 30 ppt. All tests were conducted with a water temperature of 10 °C. Corexit 9500 was applied at a dispersant to oil ratio of 1:20 in all tests.

The fresh oils were more effectively dispersed than the weathered oils that were more effectively dispersed than the weathered and emulsified oils. The most complete data sets collected were for the fresh oil tests. The results for the fresh oils indicate that the final dispersant effectiveness values are highest for the 30 ppt water and in all cases, drop as the test water salinity decreased to 5 ppt. Results were determined by skimming the surface for undispersed oil shortly after the experiment.

King et al. (2015b) elucidate the dispersion characteristics of three oil products (Canadian Cold Lake diluted bitumen, Chinese medium and heavy crude oils) treated using two chemical dispersant products (Corexit 9500 and a proprietary Chinese dispersant formulation). Experiments were conducted using breaking wave conditions generated in a wave tank facility located in Atlantic Canada. The Cold Lake diluted bitumen was effectively dispersed by Corexit 9500 under the test conditions in this study. Neither of the two dispersant products effectively dispersed the Chinese oils, especially the medium crude oil. Chemical analysis using gas chromatography/mass spectrometry revealed that the Chinese medium crude contained a greater proportion of n-alkanes (C9-C38) compared to the other oils. This product would be defined as a waxy crude, since it consists mostly of paraffin hydrocarbons (C18-C36).

King et al. (2015c) used Cold Lake Blend (CLB) diluted bitumen (Dilbit) to evaluate the fate of pre-weathered (6.2% w/w) Dilbit under environmental conditions both in spring (seawater temperature 8.5°C°C and salinity 27.7 practical salinity units [psu]) and in summer (seawater temperature 17.0°C and salinity 26.8 psu). The following oil spill treatments were considered: no treatment, dispersant alone, mineral fines (MF) alone, and dispersant plus MF. The aim was to determine their influences on the fate of spilled CLB at sea. When dispersant alone was used, the highest dispersion effectiveness (DE) was noted, and DE ranged from 45% to 59% under the selected environmental conditions. With no treatment and treatment of MF alone, CLB DE was insufficient under tested conditions. Total petroleum hydrocarbon (TPH) concentration in the water column was highest for the dispersant alone, followed by that of dispersant plus MF. TPH concentration for the dispersant alone increased abruptly with time. Droplet size distribution (DSD) resulting from dispersant alone had a unimodal shape, which was different than previously observed when conventional oils were treated with the dispersant. Cases of dispersant plus MF were thus characterized by a broader DSD compared with dispersant only and a gradual increase in TPH concentration.

Taylor et al. (2014) conducted weathering and countermeasures testing with Cold Lake Blend (CLB) and Access Western Blend (AWB) Dilbits from May 13 through May 26, 2013 at the Kinder Morgan/TransMountain Pipeline pump station in Gainford. Alberta. Based on visual observations, both Dilbits exhibited properties that one would expect of a heavy, "conventional" crude oil. In no instance was any oil observed to have sunk, during the 10-day period of testing. Densities increased as oil weathered approaching and, in some cases, exceeded 1000 kg/m^3. Viscosities increased rapidly with weathering exceeding 10,000 cP within 24 hours for both Dilbits exposed to moderate agitation. Visual observations of the surface of the oil in the various tanks showed that a crust formed as the oil weathered. Chemical analyses of the weathered oils and water column showed that concentrations of BTEX diminished rapidly although TPH values in the water column were variable and dependent on the degree of surface agitation. Countermeasures tested included dispersant application, burning, shoreline cleaners, and skimmers. Visual observations of the dispersant test revealed that Corexit 9500 was marginally effective on 6-hour weathered oil and not particularly effective for more weathered Dilbit. The test burn on 6-hour weathered oil was effective with a sustained burn and an estimated 70% oil combusted. Estimates show that approximately 50% of 24-hour weathered oil was burned, but only after sustained effort to ignite. The 72-hour weathered oil was not successfully ignited. Cleaning tests showed that removal of oil that had weathered for five days on water and then remained on tiles and exposed to air for four days, was still effective when washing substrate treated with Corexit 9580. The time oil weathered on water before being placed on the tile was less important than the time the weathered oil was exposed to air.

Results from Previous Literature Reviews

2002 Tank tests were not specifically reviewed in this study, but grouped with field trials.

2008 These were reviewed and it was noted that 17 critical factors need to be considered in any test for measuring the effectiveness of dispersants in a tank (Fingas, 2008):

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 earlier 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 behaviour and a simple comparison to an untreated control may not be valid.

3. Analytical method - There are few analytical methods that can be directly applied outside the laboratory. 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, outside of aerial microwave measurements. Thus, other values are estimations 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.Behaviour 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 a fluorometer, if such is used in the experiment) 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, but also sometimes occurs in tank tests.
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 Techniques

This section has two sub-sections, one the traditional analytical techniques associated with effectiveness measures and the second, analytical techniques broadly related to dispersant topics and not related to effectiveness measures

3.1.4.1 Analytical Techniques Related to Effectiveness

Introduction

Analytical means continues to be a major concern in measuring effectiveness. It should be made very clear that only high-quality GC/MS techniques produce a true quantitative means. 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. There needs to be more recognition that this method will always be relative and highly prone to error.

Some of the earlier test 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 hydrocarbon loss and bacterial growth. There are standard procedures published.

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). Oil does neither of these two things. Oil is a mixture of dozens to hundreds of compounds, none with a distinct 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.

There are no simply reliable means for measuring dispersant or dispersant components in water.

Summary and Conclusions

Analytical techniques as applied to dispersant effectiveness are a major issue. It should be noted that only approved ASTM or EPA chromatographic methods are considered valid for the measurement of oil in water. No spectrophotometric or fluorimetric methods will yield reliable quantitative results. These two short-cuts yield near-random and high results. There are standard ASTM methods for analysis and measurement of laboratory effectiveness.

There are no simple ways to measure dispersant in water, however there are sophisticated methods as described in the next section.

Detailed Study Summaries

ASTM (2017a,b) put out a new standard on testing in the Baffled flask. A detailed chromatographic technique is present. Similarly, a revised standard on testing with the swirling flask is also updated with a chromatographic technique. The latter standard has been in place for more than 20 years.

Cai et al. (2016) proposed the use of surface tensiometry for measuring dispersant content, however neglected the predominating effect of natural or other effects on such measurements.

Results from Previous Literature Reviews
2002 This study does not have specific analytical section, but it is noted that analytical issues are very large in many of the effectiveness methods and data.

2008 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, fluorometer were used. Studies then show that because the amount and distribution of PAHs, the target compound for fluorometer, 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 invalid colorimetric method also continues to be used in a few cases for laboratory tests.

2014 This study echoes the above statement but includes other comments: 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.

3.1.4.2 Other Analytical Aspects
Introduction

There are numerous techniques now available that relate to dispersion studies, but not directly to measuring effectiveness. Such techniques include techniques to fingerprint dispersed oil, techniques to measure dispersant components, techniques to measure physical properties of surfactants such as the critical micelle concentration, and the changes observed in the chromatograms of dispersed oil versus undispersed oil.

Summary and Conclusions

Major steps have been made in recent years in the analysis of dispersant components, especially for DOSS or bis-(2-ethylhexyl) sulfosuccinate, which is a major component of Corexit dispersants. Further, this component can now be measured in water or environmental samples such as bird eggs, down to parts per billion quantities, allowing for several important environmental fate studies. Methods have also been developed for other dispersant components such as the Tweens, Spans and solvents, however, the sensitivity is not as great. Studies in the case of the Deepwater Horizon have been able to track DOSS over dozens to hundreds of kilometers, however not so for the Tweens, Spans and solvents, leading to speculation on the fate of these particular components.

Studies on the asphaltene component of the Macondo oil enable one group of researchers to calculate that the weathering of the oil on the surface had progressed as far as a loss of 61% including that lost by dissolution in the subsurface. Others used analytical techniques to improve mass balance calculations during the DWH incident.

Specialized analytical techniques have been applied to the study of surfactants themselves and their critical micelle concentration.

Several studies have made on the effect of dispersant content on oil fingerprinting and analysis. Findings are that there are differences cause by dispersants, however higher-molecular weight biomarkers do not appear to be affected.

Detailed Study Summaries

Fu et al. (2015) reviewed the conventional UV-based methods for determining the critical micelle concentration (CMC) of surfactants which often fail for low-solubility surfactants or mixtures of surfactants/solvents or oil dispersants due to baseline uncertainty of the UV spectra. To overcome the limitations, Fu et al. (2015) proposed and tested a new UV-based approach and found that the surfactant concentration, at which the incipient red shift of the strongest UV absorbance peak of pyrene occurs, can be used to roughly locate the range of the CMC for the surfactant. They developed a method, which can accurately pinpoint the CMC graphically by following the change of the maximum measurable peak difference (i.e., the strongest UV absorbance peak minus a weaker reference peak) as a function of the surfactant concentration. Regardless of the baseline fluctuations, the method was able to accurately determine CMCs of 8 model surfactants and oil dispersants. Based on the UV-absorbance analysis, the ratio of pyrene to surfactant molecules in micelles was estimated, which further reveals the roles and abilities of various surfactants in the dissolution/dispersion of pyrene or other PAHs in water. The new method can be used to measure CMCs of a wide range of surfactants and oil dispersants.

Lewan et al. (2014) discuss the content of asphaltenes in spilled and original wellhead oils from the Deepwater Horizon (DWH) incident to provide information on the amount of original oil lost and the processes most responsible for the losses within the first 80 days of the active spill. These can provide a conservative marker for various aspects of mass balance calculations. Spilled oils were collected from open waters, coastal waters and coastal sediments during the incident. Asphaltenes are the most refractory component of crude oils but their alteration in the spilled oils during weathering prevents them from being used directly as a conservative component to calculate original oil losses. The alteration is reflected by their increase in oxygen content and depletion in ^{12}C. Experiments involving evaporation, photo-oxidation, microbial degradation, dissolution, dispersion and burning indicate that the combined effects of photo-oxidation and evaporation are responsible for these compositional changes. Based on measured losses and altered asphaltenes from these experiments, a mean of 61vol% of the original oil was lost from the surface spilled oils during the incident. This mean percentage of original oil loss is considerably larger than previous estimates of evaporative losses based on only gas chromatography (GC) amenable hydrocarbons (32-50 vol%), and highlights the importance of using asphaltenes, as well as GC amenable parameters in evaluating original oil losses and the processes responsible for the losses.

Place et al. (2016) review dispersant-in-water analysis. Although the dispersant formulations contain four classes of surfactants, current studies to date have focused on the anionic surfactant, bis-(2-ethylhexyl) sulfosuccinate (DOSS). Factors affecting the integrity of environmental and laboratory samples for Corexit analysis have not been systematically investigated. For this reason, a quantitative analytical method was developed for the detection of all four classes of surfactants, as well as the hydrolysis products of DOSS, the enantiomeric mixture of α- and β-ethylhexyl sulfosuccinate (α-/β-EHSS). The analytical method was then used to evaluate which practices for sample collection, storage, and analysis resulted in quality data. Large volume, direct injection of seawater followed by liquid chromatography tandem mass spectrometry (LC-MS/MS) minimized analytical artifacts. Concentrations of DOSS in the seawater samples ranged from 71 to 13,000 ng/L, while the nonionic surfactants including Span 80, Tween 80, Tween 85 were detected infrequently (26% of samples) at concentrations from 840 to 9100 ng/L. The enantiomers α-/β-EHSS were detected in seawater, at concentrations from 200 to 1900 ng/L, and in both Corexit dispersant formulations, indicating α-/β-EHSS were applied to the oil spill and may be not unambiguous indicators of DOSS degradation. Best practices were provided to ensure sample integrity and data quality for environmental monitoring studies.

Rosenheim et al. (2016) compiled and mapped available carbon isotope data from sedimentary organic material sampled from the Gulf of Mexico prior to 2010. These data provide a baseline to which any changes in the Gulf of Mexico after the 2010 Deepwater Horizon oil spill can be compared. The mean $\delta^{13}C$ values, relative to PDB, are -21.4 (entire Gulf of Mexico), -21.7 (shelf sediments), -20.4 (Deepwater sediments), and -25.2 (seep-affected sediments). They compare pre-spill mean $\delta^{13}C$ values to carbon isotope measurements of sedimentary organic material from coretop samples collected after the 2010 Deepwater Horizon oil spill. The differences between the mean compiled $\delta^{13}C$ values and the post-spill $\delta^{13}C$ values are corroborated by qualitative relationships with the concentration of polycyclic aromatic hydrocarbons, a proxy for oil contamination, in the sediment. The relationships between $\delta^{13}C$ of the sedimentary organic material and PAH concentrations allow estimation of background levels of PAHs on the shelf and in the deep Gulf of Mexico. Higher background levels of PAH on the shelf likely relate to Mississippi River outflow and its deposition of petrogenic PAH in riverine sediments

Song et al. (2016) examined the stability and suitability of three groups of biomarkers, i.e., sesquiterpanes, steranes, and terpanes, for Chemically-Dispersed Oil (CDO) characterization in seawater after application of a representative chemical dispersant (Corexit 9500A). The results indicated that the suitability of sesquiterpanes as biomarkers for CDO identification was affected due to less number of stable diagnostic ratios and overlapped ranges of diagnostic ratios compared to other reference oils. On the contrary, most of the steranes and terpanes could still be applied as biomarkers for CDO characterization. All the selected diagnostic ratios of terpanes were suitable for identification of oil sources. By considering both the stability and suitability, the recommended ranking of biomarkers for CDO was terpanes > steranes > sesquiterpanes.

Wang et al. studied a mixture of Huabei crude oil with Haiou 4# dispersant, and their oil fingerprint identification based on diagnosis ratios. The study used a t-test analysis to study the effect of the dispersant on the crude oil fingerprint. Firstly, GC-FID chromatograms of dispersant and 4 oil samples were compared, and the comparison result showed that the addition of dispersant influenced the chromatogram of crude oil. Secondly, the relative content of the n-alkanes (including pristane and phytane, Pr and Ph) in 4 oil samples was studied, and the result indicated that the addition of the dispersant changed the original relative content distribution of the n-alkanes' (including Pr and Ph) in crude oil. Finally, each two samples were compared by a t-test, and the results showed that the fingerprints of 4 oil samples with the addition of different amount of dispersant were different from each other, and they were different from the fingerprint of Huabei crude oil. The effects of the dispersant on C17/Pr and C18/Ph are the greatest, the influences of it on Pr/Ph and C17/C18 were greater, and its influences on (C23+C25+C27+C29)/(C24+C26+C28+C30) and (C19+C20)/(C19+C20+C21+C22) were the least. Therefore, the effect of dispersant on oil spill fingerprint identification needs to be considered on fingerprinting.

Wang et al. (2015a) studied mixtures of Fuken-2 dispersant and Bohai crude oil. Repeatability limit and t-test methods were used in this paper to analyze the influence of dispersant in oil spill identification, and calculation results of the two were compared. The results of the former showed that, in addition to C17/Pr, influenced most easily when the dispersant content in oil was large, other diagnostic ratios were still suitable for the oil added dispersant identification. The results of the latter indicated that some fingerprints of oil added dispersant were inconsistent with the original ones, especially C17/Pr and C18/Ph, so the two were no longer suitable for the oil identification. Therefore, repeatability limit, compared with t-test method, is simple and could better avoid the interference of the dispersant.

White et al. (2016) reviewed detection technologies during the Deepwater Horizon spill. Detecting oil in the northern Gulf of Mexico following the Deepwater Horizon oil spill presented unique challenges due to the spatial and temporal extent of the spill and the subsequent dilution of oil in the environment. Over time, physical, chemical, and biological processes altered the composition of the oil, further complicating its detection. Reservoir fluid, containing gas and oil, released from the Macondo well was detected in surface and subsurface environments. Oil monitoring during and after the spill required a variety of technologies, including nimble adaptation of techniques developed for non-oil-related applications. The oil detection technologies employed varied in sensitivity, selectivity, strategy, cost, usability, expertise of user, and reliability. Innovative technologies ranging from remote sensing to laboratory analytical techniques were employed and produced new information relevant to oil spill detection, including the chemical characterization, the dispersion effectiveness, and the detection limits of oil. The challenge remains to transfer these new technologies to oil spill responders so that detection of oil following a spill can be improved.

Yeudakimau et al. (2014) developed a quantification method for the determination of dioctyl sulfosuccinate sodium salt (DOSS) in avian egg samples based on a QuEChERS extraction technique followed by UPLC-MS/MS analysis. DOSS is an anionic surfactant that is part of the Corexit 9500 dispersant. QuEChERS provided a simple, effective and time saving sample preparation method prior to analysis without reducing analytical sensitivity and became an excellent substitute to lengthy traditional extraction methods. Weak anionic exchange cleanup significantly reduced matrix effects and improved analyte sensitivity. Ultra-performance liquid chromatography provided an effective separation method, while MS/MS provided the necessary selectivity and increased sensitivity. Their method achieved baseline separation of DOSS, surrogate (sodium octyl sulfate – d17) and the internal standard (sodium dioctyl sulfate – d25), with limits of detection (LOD) and limits of quantitation (LOQ) for DOSS being 260 and 500 pg/mL, respectively. Quality control recoveries were 70.5 % for the laboratory control sample and 72.4 for the matrix spike. The extraction efficiency was monitored by adding surrogate compound to every sample with recoveries of 104.6 % for SDS-d1 and 81 % for SOS-d17.

Results from Previous Literature Reviews

2014 This section was not in previous studies; however, some studies were noted in other sections of the 2014 study. Monitoring of specific dispersant components was reviewed. Dioctyl sulfosuccinate (DOSS) is a major component of the Corexit dispersants and has an aquatic toxicity of approximately double that of the whole dispersant. DOSS was found in both waters nearby and distant from areas where dispersant was used.

3.2 Toxicity to Biota

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

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.

3.2.1 Aquatic Toxicity of Dispersants with Oil

Introduction

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 often less than the toxicity of dispersed oil, but occasionally more. There are several studies departing from the traditional lethal aquatic toxicity assay and some that focus on the longer-term effects of short term exposures. There is an increasing tendency to study other than the traditional lethal assays and use some of the newer tests for genotoxicity, endocrine disruption and many sub-lethal effects. This is progress and explores the many avenues of toxicity other than simple lethality. The comparisons in this section of the report are largely between chemically-dispersed and mechanically-dispersed oil.

Summary and Conclusions

Toxicity studies in the period of 2014 to 2017 are shown in Table 1. There are more than 220 individual studies noted conducted by more than 25 separate study groups. 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 and funding. The overall summary result of these tests is that 6% of the studies where such comparison could be made, found that chemically-dispersed oil was less toxic than mechanically-dispersed oil. Seventeen (17%) of the studies where comparison could be made, noted that the chemically- and mechanically-dispersed oil had about the same toxicity. Seventy-eight (78%) percent of the studies noted that chemically-dispersed oil was more toxic than mechanically-dispersed oil. If the latter is divided into two categories, 45% showed that chemically-dispersed oil was somewhat more toxic than mechanically-dispersed oil; whereas, 33% showed that chemically-dispersed oil was much more toxic than mechanically-dispersed oil.

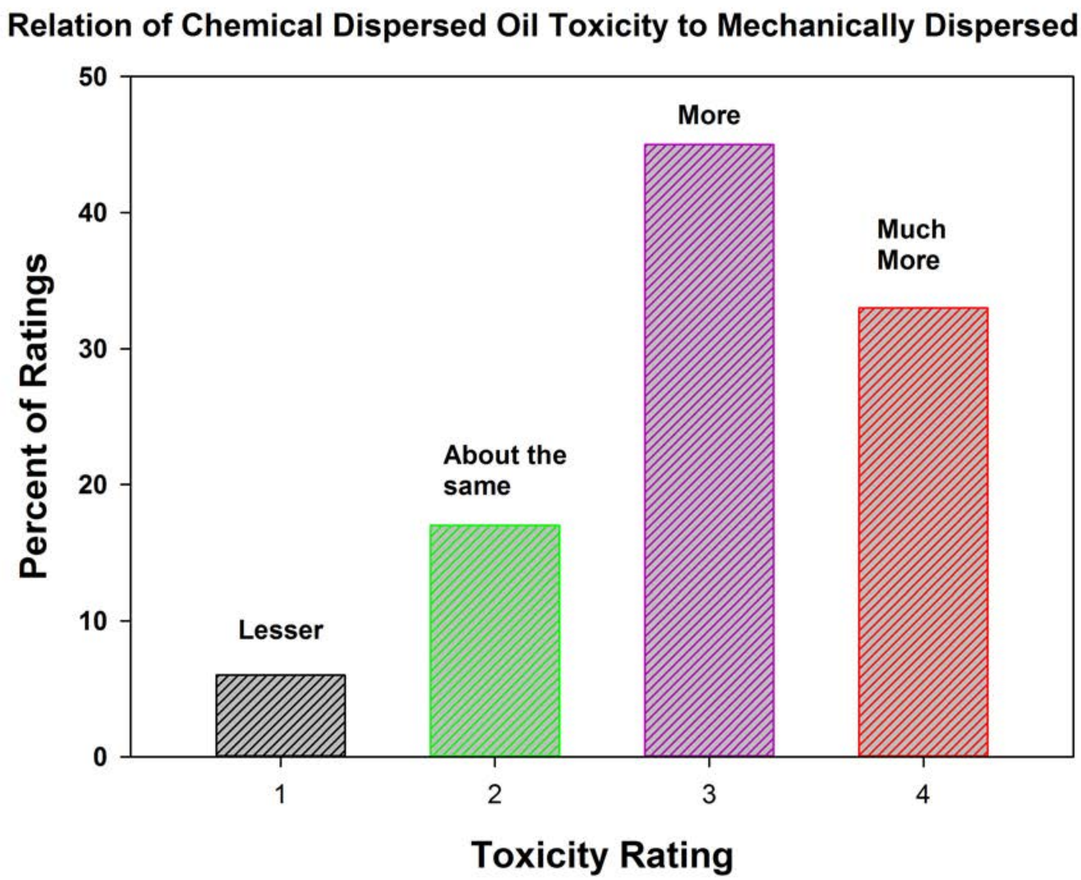

Figure 1 A summary of the toxicity ratings as graded in this review. This indicates that most of the studies reviewed found that most of the time the toxicity of the chemically-dispersed oil was greater than that of the mechanically-dispersed oil.

The many toxicity studies of water-accommodated fractions (WAF) versus chemically-enhanced water-accommodated fractions (CEWAF) show the following generalizations:

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, which may be specific to a study or if more general, these generalizations will be captured here.

c) For a few 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 most studies, it was found that CEWAF was more toxic than WAF when comparing nominal oil concentrations. The majority of these studies concluded that the addition of chemical dispersants did not change or significantly add to the toxicity of the oil but did increase the amount of oil in the water and the bioavailability of the oil chemicals, often by orders of magnitude. Studies that compare chemically and mechanically dispersed oil based on measured chemical concentrations in the water have generally demonstrated similar toxicity. However, some studies have shown that certain organisms, for example corals, are more sensitive to dispersants and chemically dispersed oil than mechanically dispersed oil.

e) Some studies showed that the CEWAF toxicity was as a result of the increase of PAHs water with CEWAF compared to WAF which results in less PAHs into the water. The increase in PAHs sometimes corresponded to the toxicity increase shown in d) 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,

h) The question of why some chemically-dispersed oil appears to be more toxic than mechanically-dispersed oil may relate to the increased amounts of PAHs in the water with chemical dispersions. This is especially true of the aquatically-toxic 2-ring and 3-ring PAHs.

i) Some workers have suggested that CEWAF is more bioavailable than mechanically-dispersed oil. This is in addition to the note in h).

j) Photo-susceptible species are particularly vulnerable to increased water concentrations of PAHs caused by chemical dispersion.

k) Juvenile forms of most species are much more susceptible to both CEWAF and WAF.

l) Although weathered oil is generally shown to be less toxic to species (chemically- or mechanically-dispersed), calculation of its PAHs may make it appears as though it is as or more toxic than un-weathered oil. It is suggested here, that irrespective of misleading calculations, that weathered oil is always less toxic than its un-weathered counterparts.

m) Some species are more susceptible to oil droplets than others, thus these species are more prone to chemically-dispersed oil than those species which are not susceptible to oil droplets.

n) Generalizations about dispersants should not be made if the dispersant itself is different from those in other studies. Many studies used Corexit 9500, however, other studies did not and in some cases used relatively unknown dispersants.

Detailed Study Summaries

Adams et al. (2014) exposed Atlantic herring (Clupea harengus) embryos water accommodated fractions (CEWAFs; oil dispersed in water with Corexit 9500A) of Medium South American (MESA) crude oil. The CEWAF was approximately 100-fold more toxic than WAF based on nominal loadings of test solutions (% v/v). The higher toxicity of CEWAFs was caused by an increase in exposure to hydrocarbons with chemical dispersion. In a second experiment, the chronic toxicity of Corexit 9500A and chemically dispersed heavy fuel oil 7102 (HFO 7102) to rainbow trout (Oncorhynchus mykiss) embryos was compared to chemically dispersed Nujol, a nontoxic mineral oil. Dispersant alone was toxic, but caused different signs of toxicity than HFO 7102. Nujol at a dispersant-to-oil ratio of 1:20 was nontoxic, suggesting that dispersant was sequestered by oil and not present at toxic concentrations. Both experiments suggest that chemically dispersed oil was more toxic to fish embryos than solutions created by mechanical mixing due to the increased exposure of fish to petroleum hydrocarbons and not to changes in hydrocarbon toxicity.

Table 1 Toxicity Studies Using Dispersant with Oil

Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Oil	Dispersant:Oil	Temp °C	Time	Result	Value	Chem species	Funder	CEWAF < WAF	CEWAF ~ WAF	CEWAF > WAF	CWAF >> WAF	Disp. Alone < WAF
Adams et al.	2014	Lab	Lethal	Atlantic Herring Embryos	Saline	Corexit 9500	Nujol	1:25	10	24 d	LC_{50}	32.5 mg/L	CEWAF	Gov't & Res.				x	
Adams et al.	2014	Lab	Lethal	Atlantic Herring Embryos	Saline		HFO	1:25	10	24 d	LC_{50}	2.50%	WAF	Gov't & Res.					
Adams et al.	2014	Lab	Sublethal	Atlantic Herring Embryos	Saline		MESA	1:25	10	24 d	EC_{50}	9.80%	WAF	Gov't & Res.					
Adams et al.	2014	Lab	Sublethal	Atlantic Herring Embryos	Saline	Corexit 9500	MESA	1:25	10	24 d	EC_{50}	2.5 mg/L	CEWAF	Gov't & Res.				x	
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - unhatched blastula	Oil only	IFO		0	48 h	EC_{50}	62 µg/L	WAF	Gov't & Res.					
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - unhatched blastula	Oil only	IFO		0	48 h	EC_{50}	71 µg/L	WAF	Gov't & Res.					
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - unhatched blastula	Dasic Slickgone NS	IFO	1:20	0	48 h	EC_{50}	5985 µg/L	CEWAF	Gov't & Res.	x				
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - unhatched blastula	Dasic Slickgone NS	IFO	1:20	0	48 h	EC_{50}	12000 µg/L	CEWAF	Gov't & Res.	x				
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - Gastrula	Oil only	IFO		0	10 d	EC_{50}	32 µg/L	WAF	Gov't & Res.					
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - Gastrula	Oil only	IFO		0	10 d	EC_{50}	340 µg/L	WAF	Gov't & Res.					
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - Gastrula	Dasic Slickgone NS	IFO	1:20	0	10 d	EC_{50}	2340 µg/L	CEWAF	Gov't & Res.	x				
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - Gastrula	Dasic Slickgone NS	IFO	1:20	0	10 d	EC_{50}	4710 µg/L	CEWAF	Gov't & Res.	x				
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - 4-armed pluteu	Oil only	IFO		0	16-18 d	EC_{50}	26 µg/L	WAF	Gov't & Res.					
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - 4-armed pluteu	Oil only	IFO		0	16-18 d	EC_{50}	98 µg/L	WAF	Gov't & Res.					
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - 4-armed pluteu	Dasic Slickgone NS	IFO	1:20	0	16-18 d	EC_{50}	2350 µg/L	CEWAF	Gov't & Res.	x				
Alexander et al	2016	Lab	Sublethal - abnormalitie	Antarctic sea Urchin	saline - life stage - 4-armed pluteu	Dasic Slickgone NS	IFO	1:20	0	16-18 d	EC_{50}	766 µg/L	CEWAF	Gov't & Res.	x				
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1812 mWs/cm²	Oil only	DWH oil		25	48 h	EC_{50}	3.7 nM/L Anth.	HEWAF	Gov't & Res.					
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1214 mWs/cm²	Oil only	DWH oil		25	48 h	EC_{50}	5.6 nM/L Anth.	HEWAF	Gov't & Res.					
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 607 mWs/cm²	Oil only	DWH oil		25	48 h	EC_{50}	11.2 nM/L Anth.	HEWAF	Gov't & Res.					
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1812 mWs/cm²	Oil only	DWH oil		25	48 h	EC_{50}	1.2 nM/L Anth.	HEWAF	Gov't & Res.					
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1214 mWs/cm²	Oil only	DWH oil		25	48 h	EC_{50}	1.8 nM/L Anth.	HEWAF	Gov't & Res.					
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 607 mWs/cm²	Oil only	DWH oil		25	48 h	EC_{50}	3.6 nM/L Anth.	HEWAF	Gov't & Res.					
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1812 mWs/cm²	Corexit 9500	DWH oil	1:10	25	48 h	EC_{50}	6.5 nM/L Anth.	HEWAF	Gov't & Res.			x		
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1214 mWs/cm²	Corexit 9500	DWH oil	1:10	25	48 h	EC_{50}	9.7 nM/L Anth.	HEWAF	Gov't & Res.			x		
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 607 mWs/cm²	Corexit 9500	DWH oil	1:10	25	48 h	EC_{50}	19.4 nM/L Anth.	HEWAF	Gov't & Res.			x		
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1812 mWs/cm²	Corexit 9500	DWH oil	1:10	25	48 h	EC_{50}	8.1 nM/L Anth.	HEWAF	Gov't & Res.			x		
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 1214 mWs/cm²	Corexit 9500	DWH oil	1:10	25	48 h	EC_{50}	12.1 nM/L Anth.	HEWAF	Gov't & Res.			x		
Alloy et al.	2016	Lab	Sub-Lethal - % hatch	Mahi-mahi embryos	Saline, Light Level - 607 mWs/cm²	Corexit 9500	DWH oil	1:10	25	48 h	EC_{50}	24.2 nM/L Anth.	HEWAF	Gov't & Res.			x		
Almeda et al.	2014	Lab	Lethal	Nauplii of Coral	Saline	Oil only	Louisiana Crude		25	72 h	LC_{50}	3.3 µL/L	WAF	Gov't & Res.					
Almeda et al.	2014	Lab	Sublethal -grow	Nauplii of Coral	Saline	Oil only	Louisiana Crude		25	72 h	EC_{50}	0.05 µL/L	WAF	Gov't & Res.					
Almeda et al.	2014	Lab	Lethal	Nauplii of Coral	Saline	Corexit 9500	Louisiana Cr	1:20	25	72 h	LC_{50}	1 µL/L	CEWAF	Gov't & Res.			x		
Almeda et al.	2014	Lab	Sublethal -grow	Nauplii of Coral	Saline	Corexit 9500	Louisiana Cr	1:20	25	72 h	EC_{50}	0.05 µL/L	CEWAF	Gov't & Res.			x		
Almeda et al.	2016a	Lab	Lethal	Nauplii of A. tonsa	Saline	Oil only	Louisiana Crude		26-30	48 h	LC_{50}	1.88 µL/L	WAF	Gov't & Res.					
Almeda et al.	2016a	Lab	Lethal	Nauplii of A. tonsa	Saline plus natural UVB light	Oil only	Louisiana Crude		26-30	48 h	LC_{50}	1.25 µL/L	WAF	Gov't & Res.					
Almeda et al.	2016a	Lab	Lethal	Nauplii of A. tonsa	Saline	Corexit 9500	Louisiana Cr	1:20	26-30	48 h	LC_{50}	<<1.88 µL/L	CEWAF	Gov't & Res.				X	

Table 1 Toxicity Studies Using Dispersant with Oil

Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Oil	Dispersant:Oil	Temp °C	Time	Result	Value	Chem species	Funder	CEWAF < WAF	CEWAF ~ WAF	CEWAF > WAF	CWAF >> WAF	Disp. Alone < WAF
Almeda et al.	2016a	Lab	Lethal	Nauplii of A. tonsa	Saline plus natural UVB light	Corexit 9500	Louisiana Cr	1:20	26-30	48 h	LC_{50}	<<1.25 µL/L	CEWAF	Gov't & Res.				x	
Almeda et al.	2016a	Lab	Lethal	Nauplii of T. turbinata	Saline	Oil only	Louisiana Crude		26-30	48 h	LC_{50}	1.95 µL/L	WAF	Gov't & Res.					
Almeda et al.	2016a	Lab	Lethal	Nauplii of T. turbinata	Saline plus natural UVB light	Oil only	Louisiana Crude		26-30	48 h	LC_{50}	1.34 µL/L	WAF	Gov't & Res.					
Almeda et al.	2016a	Lab	Lethal	Nauplii of T. turbinata	Saline	Corexit 9500	Louisiana Cr	1:20	26-30	48 h	LC_{50}	<<1.95 µL/L	CEWAF	Gov't & Res.				x	
Almeda et al.	2016a	Lab	Lethal	Nauplii of T. turbinata	Saline plus natural UVB light	Corexit 9500	Louisiana Cr	1:20	26-30	48 h	LC_{50}	<<1.34 µL/L	CEWAF	Gov't & Res.				x	
Dasgupta et al.	2015	Lab	Lethal	Larvae of Sheepshead Minnow		Corexit 9500	Louisiana Crude		27-28	48 h	toxicity > WAF		CEWAF	Gov't & Res.			x		
Dasgupta et al.	2015	Lab	Lethal	Larvae of Sheepshead Minnow		Oil only	Louisiana Crude		27-28	48 h	toxicity > CEWAF		WAF	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - C. delta	Survival %	Oil only	Macondo	1:10	5-8	96 h	Survival	90.3	Bulk oil	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - C. delta	Survival %	Dispersant	Macondo	1:10	5-8	96 h	Survival	93.5	Dispersant	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - C. delta	Survival %	CEWAF	Macondo	1:10	5-8	96 h	Survival	90.5	CEWAF	Gov't & Res.			x		
DeLeo et al.	2016	Lab	Lethal	Coral - C. delta	Survival %	Oil only	Macondo	1:10	5-8	96 h	Survival	93.5	WAF	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - C. delta	Survival %	Dispersant	Macondo	1:10	5-8	96 h	Survival	89.1	Dispersant	Gov't & Res.					x
DeLeo et al.	2016	Lab	Lethal	Coral - C. delta	Survival %	CEWAF	Macondo	1:10	5-8	96 h	Survival	92.3	CEWAF	Gov't & Res.			x		
DeLeo et al.	2016	Lab	Lethal	Coral - Paramuricea B3	Survival %	Oil only	Macondo	1:10	5-8	96 h	Survival	91.9	Bulk oil	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - Paramuricea B3	Survival %	Dispersant	Macondo	1:10	5-8	96 h	Survival	93.5	Dispersant	Gov't & Res.					x
DeLeo et al.	2016	Lab	Lethal	Coral - Paramuricea B3	Survival %	CEWAF	Macondo	1:10	5-8	96 h	Survival	87.6	CEWAF	Gov't & Res.			x		
DeLeo et al.	2016	Lab	Lethal	Coral - Paramuricea B3	Survival %	Oil only	Macondo	1:10	5-8	96 h	Survival	96	WAF	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - Paramuricea B3	Survival %	Dispersant	Macondo	1:10	5-8	96 h	Survival	82.5	Dispersant	Gov't & Res.					x
DeLeo et al.	2016	Lab	Lethal	Coral - Paramuricea B3	Survival %	CEWAF	Macondo	1:10	5-8	96 h	Survival	94.5	CEWAF	Gov't & Res.			x		
DeLeo et al.	2016	Lab	Lethal	Coral - L. glaberrima	Survival %	Oil only	Macondo	1:10	5-8	96 h	Survival	95.4	Bulk oil	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - L. glaberrima	Survival %	Dispersant	Macondo	1:10	5-8	96 h	Survival	96	Dispersant	Gov't & Res.					x
DeLeo et al.	2016	Lab	Lethal	Coral - L. glaberrima	Survival %	CEWAF	Macondo	1:10	5-8	96 h	Survival	91	CEWAF	Gov't & Res.			x		
DeLeo et al.	2016	Lab	Lethal	Coral - L. glaberrima	Survival %	Oil only	Macondo	1:10	5-8	96 h	Survival	96	WAF	Gov't & Res.					
DeLeo et al.	2016	Lab	Lethal	Coral - L. glaberrima	Survival %	Dispersant	Macondo	1:10	5-8	96 h	Survival	77.8	Dispersant	Gov't & Res.					x
DeLeo et al.	2016	Lab	Lethal	Coral - L. glaberrima	Survival %	CEWAF	Macondo	1:10	5-8	96 h	Survival	86.4	CEWAF	Gov't & Res.			x		
Dussauze et al.	2014	Lab	Sub-Lethal	Sea Bass	Respiratory effects	Finasol OSR 52	Arabian L	1:20	13.9	48 h	Gross Effe	disperant alone decreased respira		Gov't & Res.					x
Dussauze et al.	2014	Lab	Sub-Lethal	Arctic Cod	Respiratory effects		Arabian Lt.		13.9	48 h	Gross Effe	Oil alone decreased respiration		Gov't & Res.					
Dussauze et al.	2015a	Lab	Sub-Lethal	Sea Bass	Growth and virus Immunity	Finasol OSR 62	Arabian L	1:20	17.3	3 d + 12	growth not affected, immunity initially in 12			Industry					
Dussauze et al.	2015b	Lab	Sub-Lethal	Sea Bass	Hormone levels and health	Oil only	Arabian Lt.		16	48 h	Some effects, similar hormon		WAF	Industry					
Dussauze et al.	2015b	Lab	Sub-Lethal	Sea Bass	Hormone levels and health	Corexit 9500	Arabian L	1:20	16	48 h	<lysozyme conc., tissue dama		CEWAF	Industry			x		
Dussauze et al.	2015c	Lab	Lethal	Sea Bass	Lethality of CEWAFs	4 different	Arabian L	1:20	16	24-96	same lethality to calc. oil		CEWAF	Industry			x		
Dussauze et al.	2016	Lab	Sub-Lethal	Sea Bass	Survivability with pressure change	Control	Arabian L	1:20	17.4	48 h	Prob. of de	0.13	Control	Industry					
Dussauze et al.	2016	Lab	Sub-Lethal	Sea Bass	Survivability with pressure change	Finasol OSR 52	Arabian L	1:20	17.4	48 h	Prob. of de	0.08	Dispersant	Industry			x		
Dussauze et al.	2016	Lab	Sub-Lethal	Sea Bass	Survivability with pressure change	Oil only	Arabian L	1:20	17.4	48 h	Prob. of de	0.16	WAF	Industry					
Dussauze et al.	2016	Lab	Sub-Lethal	Sea Bass	Survivability with pressure change	Finasol OSR 52	Arabian L	1:20	17.4	48 h	Prob. of de	0.19	CEWAF 50 mg/l	Industry			x		
Dussauze et al.	2016	Lab	Sub-Lethal	Sea Bass	Survivability with pressure change	Finasol OSR 52	Arabian L	1:20	17.4	48 h	Prob. of de	0.26	CEWAF 80 mg/l	Industry			x		
Echols et al.	2016	Lab	Lethal	Ephyrae of jellyfish	Lethality	Corexit 9500		1:20	25	96 h	LC_{50}	32.3 mg/L	Dispersant onl	Industry					x
Echols et al.	2016	Lab	Lethal	Ephyrae of jellyfish	Lethality	unweathered	Macondo	1:20	25	96 h	LC_{50}	>21.1 mg/L	WAF	Industry					
Echols et al.	2016	Lab	Lethal	Ephyrae of jellyfish	Lethality	weathered oil	Macondo	1:20	25	96 h	LC_{50}	>152.2 mg/L	WAF	Industry					
Echols et al.	2016	Lab	Lethal	Ephyrae of jellyfish	Lethality	Corexit 9500	Macondo	1:20	25	96 h	LC_{50}	<181 mg/L	CEWAF	Industry			x		
Elarbaoui et al.	2015	esoco	Sub-Lethal	Benthic Organisms	Species count in various treatme	Finasol OSR 52	Arabian L	1:20	19	2- d	#'s biota	Species reacted	Disp., Oil a	Gov't & Res.			x		

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Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Oil	Dispersant:Oil	Temp °C	Time	Result	Value	Chem species	Funder	CEWAF < WAF	CEWAF ~ WAF	CEWAF > WAF	CWAF >> WAF	Disp. Alone < WAF
Esbaugh et al.	2016	Lab	Lethal	Mahi-mahi	Lethality	unweathered	Macondo		26	96 h	LC_{50}	45.8 µg/L PAHs	WAF	Gov't & Res.					
Esbaugh et al.	2016	Lab	Lethal	Mahi-mahi	Lethality	weathered oil	Macondo		26	96 h	LC_{50}	12.3 µg/L PAHs	WAF	Gov't & Res.					
Esbaugh et al.	2016	Lab	Lethal	Mahi-mahi	Lethality	Slick oil	Macondo		26	96 h	LC_{50}	8.8 µg/L PAHs	WAF	Gov't & Res.					
Esbaugh et al.	2016	Lab	Lethal	Mahi-mahi	Lethality	Corexit 9500	Macondo	1:10	26	96 h	LC_{50}	25.3 µg/L PAHs	Unweathered	Gov't & Res.	x				
Esbaugh et al.	2016	Lab	Lethal	Mahi-mahi	Lethality	Corexit 9500	Macondo	1:10	26	96 h	LC_{50}	8.7 µg/L PAHs	Weathered	Gov't & Res.	x				
Esbaugh et al.	2016	Lab	Lethal	Mahi-mahi	Lethality	Corexit 9500	Macondo	1:10	26	96 h	LC_{50}	9.5 µg/L PAHs	Slick oil	Gov't & Res.	x				
Esbaugh et al.	2016	Lab	Lethal	Mahi-mahi	Lethality	Corexit 9500			26	96 h	LC_{50}	3.9 µg/L PAHs	Dispersant On	Gov't & Res.				x	
Esbaugh et al.	2016	Lab	Sub-Lethal	Mahi-mahi	Sub-Lethal - pericardial edema	unweathered	Macondo		26	48 h	EC_{50}	7.3 µg/L PAHs	WAF	Gov't & Res.					
Esbaugh et al.	2016	Lab	Sub-Lethal	Mahi-mahi	Sub-Lethal - pericardial edema	weathered oil	Macondo		26	48 h	EC_{50}	5.7 µg/L PAHs	WAF	Gov't & Res.					
Esbaugh et al.	2016	Lab	Sub-Lethal	Mahi-mahi	Sub-Lethal - pericardial edema	Slick oil	Macondo		26	48 h	EC_{50}	> 5.1 µg/L PAHs	WAF	Gov't & Res.					
Esbaugh et al.	2016	Lab	Sub-Lethal	Mahi-mahi	Sub-Lethal - pericardial edema	Corexit 9500	Macondo	1:10	26	48 h	EC_{50}	11.5 µg/L PAHs	Unweathered	Gov't & Res.	x				
Esbaugh et al.	2016	Lab	Sub-Lethal	Mahi-mahi	Sub-Lethal - pericardial edema	Corexit 9500	Macondo	1:10	26	48 h	EC_{50}	11.3 µg/L PAHs	Weathered	Gov't & Res.	x				
Esbaugh et al.	2016	Lab	Sub-Lethal	Mahi-mahi	Sub-Lethal - pericardial edema	Corexit 9500	Macondo	1:10	26	48 h	EC_{50}	13 µg/L PAHs	Slick oil	Gov't & Res.	x				
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Mechanically	Troll		4.2-6.9	24 h	EC_{50}	22.1 µg/g	basis naphthaler	Industry					
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Mechanically	Troll		4.2-6.9	24 h	EC_{50}	45.1 µg/g	basis 16 PAHs	Industry					
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Mechanically	Troll		4.2-6.9	48 h	EC_{50}	24.7 µg/g	basis naphthaler	Industry					
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Mechanically	Troll		4.2-6.9	48 h	EC_{50}	40.9 µg/g	basis 16 PAHs	Industry					
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Dasic Slickgone	Troll	1:25	4.2-6.9	24 h	EC_{50}	21.5 µg/g	basis naphthaler	Industry	x				
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Dasic Slickgone	Troll	1:25	4.2-6.9	24 h	EC_{50}	51.5 µg/g	basis 16 PAHs	Industry	x				
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Dasic Slickgone	Troll	1:25	4.2-6.9	48 h	EC_{50}	19.1 µg/g	basis naphthaler	Industry	x				
Frantzen et al.	2015	Lab	Sub-Lethal	Lump Sucker juveniles	Sub-Lethal - Narcosis	Dasic Slickgone	Troll	1:25	4.2-6.9	48 h	EC_{50}	47.2 µg/g	basis 16 PAHs	Industry	x				
Frantzen et al.	2015	Lab	Lethal	Lump Sucker juveniles	Lethality	Dasic Slickgone	Troll	1:25	4.2-6.9	24 h	LC_{50}	120 µg/g	basis naphthaler	Industry	x				
Frantzen et al.	2015	Lab	Lethal	Lump Sucker juveniles	Lethality	Dasic Slickgone	Troll	1:25	4.2-6.9	24 h	LC_{50}	223 µg/g	basis 16 PAHs	Industry	x				
Frantzen et al.	2015	Lab	Lethal	Lump Sucker juveniles	Lethality	Dasic Slickgone	Troll	1:25	4.2-6.9	48 h	LC_{50}	103 µg/g	basis naphthaler	Industry	x				
Frantzen et al.	2015	Lab	Lethal	Lump Sucker juveniles	Lethality	Dasic Slickgone	Troll	1:25	4.2-6.9	48 h	LC_{50}	191 µg/g	basis 16 PAHs	Industry	x				
Frantzen et al.	2016	Lab	Lethal	Scallops	Lethality	Dasic Slickgone	Troll	1:25	4.2-6.9	48 h	Mechanically and Chemically dispersed simi			Industry	x				
Hansen et al.	2015	Lab	Sub-lethal - egg	Juvenile Copepods	Number of eggs produced	Dasic Slickgone	Troll	1:25	10	1-15 d	# s egg	16.3	Chemical disp.	ND		x			
Hansen et al.	2015	Lab	Sub-lethal - egg	Juvenile Copepods	Number of eggs produced	Dasic Slickgone	Troll	1:25	10	1-15 d	# s egg	17.1	Mech. Disp.	ND					
Hansen et al.	2015	Lab	Sub-lethal - egg	Juvenile Copepods	Number of eggs produced	Dasic Slickgone	Troll	1:25	10	16-25 d	# s egg	19.3	Chemical disp.	ND		x			
Hansen et al.	2015	Lab	Sub-lethal - egg	Juvenile Copepods	Number of eggs produced	Dasic Slickgone	Troll	1:25	10	16-25 d	# s egg	34.3	Mech. Disp.	ND					
Laramore et al.	2014	Lab	Sub-Lethal - various	Larval Oysters	Decreased fertilization	Corexit 9500	Macondo	1:10	26	most <96	LOEL	> 100 mg/L	CEWAF	Gov't & Res.			x		
Laramore et al.	2014	Lab	Sub-Lethal - various	Larval Oysters	Hinder trocophore		Macondo		26	most <96	LOEL	> 100 mg/L	WAF	Gov't & Res.					
Laramore et al.	2014	Lab	Sub-Lethal - various	Larval Oysters	Hinder trocophore	Corexit 9500	Macondo	1:10	26	most <96	LOEL	> 12.5 mg/L	CEWAF	Gov't & Res.			x		
Laramore et al.	2014	Lab	Sub-Lethal - various	Larval Oysters	Hinder D-Stage Development	Corexit 9500	Macondo	1:10	26	most <96	LOEL	> 100 mg/L	CEWAF or WAF	Gov't & Res.	x				
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage		Macondo		26	24 h	LC_{50}	1090 mg/L	WAF	Gov't & Res.					
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage		Macondo		26	48 h	LC_{50}	554 mg/L	WAF	Gov't & Res.					
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage		Macondo		26	72 h	LC_{50}	289 mg/L	WAF	Gov't & Res.					
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage		Macondo		26	96 h	LC_{50}	262 mg/L	WAF	Gov't & Res.					
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage	Corexit 9500	Macondo	1:10	26	24 h	LC_{50}	178 mg/L	CEWAF	Gov't & Res.			x		
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage	Corexit 9500	Macondo	1:10	26	48 h	LC_{50}	44.7 mg/L	CEWAF	Gov't & Res.			x		
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage	Corexit 9500	Macondo	1:10	26	72 h	LC_{50}	33.8 mg/L	CEWAF	Gov't & Res.			x		
Laramore et al.	2014	Lab	Lethal	Larval Oysters	Lethality D-Stage	Corexit 9500	Macondo	1:10	26	96 h	LC_{50}	24.8 mg/L	CEWAF	Gov't & Res.			x		

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Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Oil	Dispersant:Oil	Temp °C	Time	Result	Value	Chem species	Funder	CEWAF < WAF	CEWAF ~ WAF	CEWAF > WAF	CWAF >> WAF	Disp. Alone < WAF	
Mauduit et al.	2016	) + Me	Exp. Plus recov	European Sea Bass	saline	Corexit 9500	Arabian L	1:25	9-20	48 h	impairment		oil, dispersant	Gov't & Ind.						
Mu et al.	2014	Lab	Sub-Lethal, Chron	Larval Medaka	Blue Sac Disease		Heavy Zuata		26	25 d	EC_{20}	0.56 mg/L	WAF	ND						
Mu et al.	2014	Lab	Sub-Lethal, Chron	Larval Medaka	Blue Sac Disease	Shuang Chemical	Heavy Zu	1:10	26	25 d	EC_{20}	0.78 mg/L	CEWAF	ND				x		
Mu et al.	2014	Lab	Sub-Lethal, Chron	Larval Medaka	Blue Sac Disease	Weipou - Biological	Heavy Zu	1:10	26	25 d	EC_{20}	5.6 mg/L	BEWAF	ND				x		
Mu et al.	2014	Lab	Sub-Lethal, Chron	Larval Medaka	Blue Sac Disease		Heavy Zuata		26	25 d	EC_{20}	22.5 mg/L	WAF as PAHs	ND						
Mu et al.	2014	Lab	Sub-Lethal, Chron	Larval Medaka	Blue Sac Disease	Shuang Chemical	Heavy Zu	1:10	26	25 d	EC_{20}	13.4 mg/L	CEWAF as PAH	ND				x		
Mu et al.	2014	Lab	Sub-Lethal, Chron	Larval Medaka	Blue Sac Disease	Weipou - Biological	Heavy Zu	1:10	26	25 d	EC_{20}	24.7 mg/L	BEWAF as PAH	ND						
Muncaster et al	2016	Lab	Lethal	Larval Kingfish	Lethality		HFO Rena		20	24 h	LC_{50}	1 µg/L	WAF as PAHs	Gov't & Res.						
Muncaster et al	2016	Lab	Lethal	Larval Kingfish	Lethality	Corexit 9500	HFO Rena	1:20	20	24 h	LC_{50}	< 1 µg/L	CEWAF as PAH	Gov't & Res.				x		
Muncaster et al	2016	Lab	Lethal	Larval Kingfish	Lethality	Corexit 9500	HFO Rena	1:20	20	24 h	LC_{100}	0.3 µg/L	CEWAF as PAH	Gov't & Res.				x		
Muncaster et al	2016	Lab	Lethal	Larval Kingfish	Lethality		HFO Rena		20	24 h	$LC_{35.5}$	0.2 µg/L	WAF as PAHs	Gov't & Res.						
Muncaster et al	2016	Lab	Lethal	Larval Kingfish	Lethality		HFO Rena		20	24 h	LC_{53}	0.3 µg/L	WAF as PAHs	Gov't & Res.						
Muncaster et al	2016	Lab	Lethal	Larval Kingfish	Lethality		HFO Rena		20	24 h	LC_{84}	1.5 µg/L	WAF as PAHs	Gov't & Res.						
Nordtug et al.	2015	Lab	Sub-Lethal	*Calanus finmarchicus*	Filtratration		Troll		10	96 h	Filtration	Filtration reduced	WAF	Industry						
Nordtug et al.	2015	Lab	Sub-Lethal	*Calanus finmarchicus*	Filtratration	Dasic Slickgone	Troll	1:25	10	96 h	Filtration	Reduced more	CEWAF	Industry			x			
Nørregaard et al.	2015	Lab	Sub-Lethal	*Calanus hyperboreus*	Egg production and observation		Corn oil	1:20	4	76 d	Egg produc	similar	WAF as PAHs	Gov't & Res.						
Nørregaard et al.	2015	Lab	Sub-Lethal	*Calanus hyperboreus*	Egg production and observati	Agma	Corn oil	1:20	4	76 d	Egg produc	similar but slight tc	CEWAF as PAH	Gov't & Res.		x				
Nwaizuzu et al.	2015	Lab	Lethal	African Catfish	Lethality and observatior	Seacare	Bonny Light			96 h	LC_{50}	199 mg/L	CEWAF	ND				x		
Nwaizuzu et al.	2015	Lab	Lethal	African Catfish	Lethality and observatior	Seacare	Bonny Light			96 h	LC_{0}	<199 mg/L	CEWAF	ND				x		
Olsen et al.	2016	Lab	Lethal	amphipod *Eurythenes*	Lethality	Finasol	Arabian Lt.	1:20	1	24 h	LC_{50}	101 mg/L	CEWAF	Industry			x			
Olsen et al.	2016	Lab	Lethal	amphipod *Eurythenes*	Lethality	Finasol	Arabian Lt.	1:20	1	72 h	LC_{50}	24 mg/L	CEWAF	Industry			x			
Olsen et al.	2016	Lab	Lethal	amphipod *Eurythenes*	Lethality	Finasol	Arabian Lt.	1:20	1	96 h	LC_{50}	12 mg/L	CEWAF	Industry			x			
Overholt et al.	2016	Lab	Lethal	Uninoculated control	Lethality to Rotifer (EPA test)	Corexit 9500	Marlin	1:50	25	96 h	LC_{50}	75.1 µg/ml	Dispersant onl	Gov't & Res.					x	
Overholt et al.	2016	Lab	Lethal	0.01% Corexit + Alcanivorax	Lethality to Rotifer (EPA test)	Corexit 9500	Marlin	1:50	25	96 h	LC_{50}	83.8 µg/ml	Dispersant onl	Gov't & Res.					x	
Overholt et al.	2016	Lab	Lethal	0.01% Corexit + Acinetobacter	Lethality to Rotifer (EPA test)	Corexit 9500	Marlin	1:50	25	96 h	LC_{50}	82.9 µg/ml	Dispersant onl	Gov't & Res.					x	
Overholt et al.	2016	Lab	Lethal	Uninoculated control	Lethality to Rotifer (EPA test)	Corexit 9500	Marlin	1:50	25	96 h	LC_{50}	27.7 % CEWAF	CEWAF	Gov't & Res.			x			
Overholt et al.	2016	Lab	Lethal	CEWAF + Alcanivorax	Lethality to Rotifer (EPA test)	Corexit 9500	Marlin	1:50	25	96 h	LC_{50}	87.5 % CEWAF	CEWAF	Gov't & Res.			x			
Overholt et al.	2016	Lab	Lethal	CEWAF + Acinetobacter	Lethality to Rotifer (EPA test)	Corexit 9500	Marlin	1:50	25	96 h	LC_{50}	83 % CEWAF	CEWAF	Gov't & Res.			x			
Overholt et al.	2016	Lab	Lethal	Uninoculated control	Lethality to Rotifer (EPA test)	Oil only	Marlin		25	96 h	LC_{50}	ND	WAF	Gov't & Res.						
Overholt et al.	2016	Lab	Lethal	WAF + Alcanivorax	Lethality to Rotifer (EPA test)	Oil only	Marlin		25	96 h	LC_{50}	ND	WAF	Gov't & Res.						
Overholt et al.	2016	Lab	Lethal	WAF + Acinetobacter	Lethality to Rotifer (EPA test)	Oil only	Marlin		25	96 h	LC_{50}	93 % WAF	WAF	Gov't & Res.						
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metabolic	Corexit 9500			15	24 h	LC_{50}	9.5 mg/L	Dispersant onl	Gov't & Res.					x	
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metabolic	Corexit 9500			15	48 h	LC_{50}	8.1 mg/L	Dispersant onl	Gov't & Res.					x	
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metabolic	Corexit 9500			23	24 h	LC_{50}	18.9 mg/L	Dispersant onl	Gov't & Res.					x	
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metabolic		Louisiana Crude		15	48 h	LC_{50}	29.5 mg/L	Oil only - WAF	Gov't & Res.						
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metabolic		Louisiana Crude		23	24 h	LC_{50}	4.7 mg/L	Oil only - WAF	Gov't & Res.						
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metaboli	Corexit 9500	iisiana Crı	1:10	15	24 h	LC_{50}	13.4 mg/L	CEWAF	Gov't & Res.			x			
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metaboli	Corexit 9500	iisiana Crı	1:10	15	48 h	LC_{50}	6.7 mg/L	CEWAF	Gov't & Res.			x			
Peiffer and Coher	2015	Lab	Lethal	ctenophore	Lethality and metaboli	Corexit 9500	iisiana Crı	1:10	23	24 h	LC_{50}	7.7 mg/L	CEWAF	Gov't & Res.			x			
Redman et al.	2017	Lab	Acute (GC X GC)	*Daphnia magna*	Effect of droplets - CEWAF	Corexit 9500	Endicott	1:10	20	48 h	LC_{50}	1.4 µg/L	CEWAF	Industry			x			
Redman et al.	2017	Lab	Acute (GC X GC)	*Daphnia magna*	Effect of droplets - WAF (PDWAF)		Endicott		20	48 h	LC_{50}	1.9 µg/L	WAF	Industry						
Redman et al.	2017	Lab	Acute (GC X GC)	*Daphnia magna*	Effect of droplets - passive WAF		Endicott		20	48 h	LC_{50}	1.7 µg/L	WAF dissolv	Industry						

Table 1 Toxicity Studies Using Dispersant with Oil

Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Oil	Dispersant:Oil	Temp °C	Time	Result	Value	Chem species	Funder	CEWAF < WAF	CEWAF ~ WAF	CEWAF > WAF	CWAF >> WAF	Disp. Alone < WAF
Redman et al.	2017	Lab	Acute (Conven)	*Daphnia magna*	Effect of droplets - CEWAF	Corexit 9500	Endicott	1:10	20	48 h	LC_{50}	0.26 µg/L	CEWAF	Industry			x		
Redman et al.	2017	Lab	Acute (Conven)	*Daphnia magna*	Effect of droplets - WAF (PDWAF)		Endicott		20	48 h	LC_{50}	0.20 µg/L	WAF	Industry					
Redman et al.	2017	Lab	Acute (Conven)	*Daphnia magna*	Effect of droplets - passive WAF		Endicott		20	48 h	LC_{50}	0.37 µg/L	WAF dissolved	Industry					
Redman et al.	2017	Lab	Acute (GC X GC)	Mysid - *Americamysis bahic*	Effect of droplets - CEWAF	Corexit 9500	Endicott	1:10	20	48 h	LC_{50}	3.6 µg/L	CEWAF	Industry			x		
Redman et al.	2017	Lab	Acute (GC X GC)	Mysid - *Americamysis bahic*	Effect of droplets - WAF (PDWAF)		Endicott		20	48 h	LC_{50}	2.9 µg/L	WAF	Industry					
Redman et al.	2017	Lab	Acute (GC X GC)	Mysid - *Americamysis bahic*	Effect of droplets - passive WAF		Endicott		20	48 h	LC_{50}	4.7 µg/L	WAF dissolv	Industry					
Redman et al.	2017	Lab	Acute (Conven)	Mysid - *Americamysis bahic*	Effect of droplets - CEWAF	Corexit 9500	Endicott	1:10	20	48 h	LC_{50}	0.42 µg/L	CEWAF	Industry			x		
Redman et al.	2017	Lab	Acute (Conven)	Mysid - *Americamysis bahic*	Effect of droplets - WAF (PDWAF)		Endicott		20	48 h	LC_{50}	0.96 µg/L	WAF	Industry					
Redman et al.	2017	Lab	Acute (Conven)	Mysid - *Americamysis bahic*	Effect of droplets - passive WAF		Endicott		20	48 h	LC_{50}	0.42 µg/L	WAF dissolv	Industry					
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathele*	Lethal and Growth	Local Philippines	Bunker C	1:9	17-29	72 h	EC_{50}	3.30%	CEWAF	Gov't & Res.					
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Local Philippines			17-29	72 h	EC_{50}	2.40%	Dispersant C	Gov't & Res.				x	
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Local Philippines	Bunker C	1:9	17-29	72 h	NOEC	3%	CEWAF	Gov't & Res.					x
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Local Philippines	Bunker C	1:9	17-29	72 h	LOEC	2%	CEWAF	Gov't & Res.				x	
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Local Philippines		1:9	17-29	72 h	NOEC	2%	Dispersant On	Gov't & Res.					x
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Local Philippines		1:9	17-29	72 h	LOEC	1%	Dispersant On	Gov't & Res.					x
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Oil only	Bunker C		17-29	72 h	EC_{50}	> 3 %	WAF	Gov't & Res.					
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Oil only	Bunker C		17-29	72 h	NOEC	> 3 %	WAF	Gov't & Res.					
Santander-Avanceña e	2016	Lab	Acute and Sublethal	Algae- *Tetraselmis tetrathe*	Lethal and Growth	Oil only	Bunker C		17-29	72 h	LOEC	> 3 %	WAF	Gov't & Res.					
Tissier et al.	2015	Lab	Sublethal Respiratory	Sea Bass - *Dicentrarchus labra*	Various Respiratory Pa	Control			13.9	72 h	Resp. O	1.15 µmol O_2	Control	Industry					
Tissier et al.	2015	Lab	Sublethal Respiratory	Sea Bass - *Dicentrarchus la*	Various Respiratory Pa	Finasol OSR 52			13.9	72 h	Resp. O	0.47 µmol O_2	Dispersant onl	Industry					x
Tissier et al.	2015	Lab	Sublethal Respiratory	Sea Bass - *Dicentrarchus la*	Various Respiratory Pa	Finasol OSR 52	Arabian L	1:20	13.9	72 h	Resp. O	0.89 µmol O_2	CEWAF	Industry			x		
Tissier et al.	2015	Lab	Sublethal Respirato	Sea Bass - *Dicentrarchus la*	Various Respiratory Parameters		Arabian Lt.		13.9	72 h	Resp. O	1.25 µmol O_2	WAF	Industry					
Vignier et al.	2015	Lab	Sublethal	Oyster Larvae	Fertilization success		Macondo		26	1 h	EC_{20}	1650 µg tPAH	HEWAF	Gov't & Res.					
Vignier et al.	2015	Lab	Sublethal	Oyster Larvae	Fertilization success	Corexit 9500	Macondo	1:10	26	1 h	EC_{20}	19.4 µg tPAH	CEWAF	Gov't & Res.				x	
Vignier et al.	2015	Lab	Sublethal	Oyster Larvae	Fertilization success	Corexit 9500			26	1 h	EC_{20}	6.9 mg	Dispersant onl	Gov't & Res.					x
Vignier et al.	2015	Lab	Sublethal	Oyster Larvae	Fertilization success		Macondo		26	1 h	EC_{50}	2250 µg tPAH	HEWAF	Gov't & Res.					
Vignier et al.	2015	Lab	Sublethal	Oyster Larvae	Fertilization success	Corexit 9500	Macondo	1:10	26	1 h	EC_{50}	29.9 µg tPAH	CEWAF	Gov't & Res.				x	
Vignier et al.	2015	Lab	Sublethal	Oyster Larvae	Fertilization success	Corexit 9500			26	1 h	EC_{50}	11.5 mg	Dispersant onl	Gov't & Res.					x
Vignier et al.	2015	Lab	Sublethal	Oyster Gametes	Observed abnormalities		Macondo		26	1 h	EC_{20}	186 µg tPAH	HEWAF	Gov't & Res.					
Vignier et al.	2015	Lab	Sublethal	Oyster Gametes	Observed abnormalities	Corexit 9500	Macondo	1:10	26	1 h	EC_{20}	9.7 µg tPAH	CEWAF	Gov't & Res.				x	
Vignier et al.	2015	Lab	Sublethal	Oyster Gametes	Observed abnormalities	Corexit 9500			26	1 h	EC_{20}	7.39 mg	Dispersant onl	Gov't & Res.					x
Vignier et al.	2015	Lab	Sublethal	Oyster Gametes	Observed abnormalities		Macondo		26	1 h	EC_{50}	267 µg tPAH	HEWAF	Gov't & Res.					
Vignier et al.	2015	Lab	Sublethal	Oyster Gametes	Observed abnormalities	Corexit 9500	Macondo	1:10	26	1 h	EC_{50}	14.9 µg tPAH	CEWAF	Gov't & Res.				x	
Vignier et al.	2015	Lab	Sublethal	Oyster Embryos	Observed abnormalities		Macondo		26	1 h	EC_{20}	218 µg tPAH	HEWAF	Gov't & Res.					
Vignier et al.	2015	Lab	Sublethal	Oyster Embryos	Observed abnormalities	Corexit 9500	Macondo	1:10	26	1 h	EC_{20}	12.2 µg tPAH	CEWAF	Gov't & Res.				x	
Vignier et al.	2015	Lab	Sublethal	Oyster Embryos	Observed abnormalities	Corexit 9500			26	1 h	EC_{20}	5.3 mg	Dispersant onl	Gov't & Res.					x
Vignier et al.	2015	Lab	Sublethal	Oyster Embryos	Observed abnormalities		Macondo		26	1 h	EC_{50}	342 µg tPAH	HEWAF	Gov't & Res.					
Vignier et al.	2015	Lab	Sublethal	Oyster Embryos	Observed abnormalities	Corexit 9500	Macondo	1:10	26	1 h	EC_{50}	15.6 µg tPAH	CEWAF	Gov't & Res.				x	
Vignier et al.	2015	Lab	Sublethal	Oyster Embryos	Observed abnormalities	Corexit 9500			26	1 h	EC_{50}	5.67 mg	Dispersant onl	Gov't & Res.					x
Vignier et al.	2016	Lab	Acute	Oyster - 1-day	saline, oil only	Oil only	DWH		25.5	96 h	EC_{50}	715 µg/L	HEWAF	Gov't & Res.					
Vignier et al.	2016	Lab	Acute	Oyster - 7-day	saline, oil only	Oil only	DWH		25.5	96 h	EC_{50}	2814 µg/L	HEWAF	Gov't & Res.					
Vignier et al.	2016	Lab	Acute	Oyster - 14-day	saline, oil only	Oil only	DWH		25.5	96 h	EC_{50}	1530 µg/L	HEWAF	Gov't & Res.					

Table 1 Toxicity Studies Using Dispersant with Oil

Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Oil	Dispersant:Oil	Temp °C	Time	Result	Value	Chem species	Funder	CEWAF < WAF	CEWAF ~ WAF	CEWAF > WAF	CWAF >> WAF	Disp. Alone < W
Vignier et al.	2016	Lab	Acute	Oyster - 1-day	saline, expressed as disp	Corexit 9500	DWH	1:10	25.5	96 h	EC_{50}	22.5 μg/L	CEWAF	Gov't & Res.			x		
Vignier et al.	2016	Lab	Acute	Oyster - 7-day	saline, expressed as disp	Corexit 9500	DWH	1:10	25.5	96 h	EC_{50}	39.6 μg/L	CEWAF	Gov't & Res.			x		
Vignier et al.	2016	Lab	Acute	Oyster - 14-day	saline, expressed as disp	Corexit 9500	DWH	1:10	25.5	96 h	EC_{50}	26 μg/L	CEWAF	Gov't & Res.			x		
Vignier et al.	2016	Lab	Acute	Oyster - 1-day	saline, expressed as oil	Corexit 9500	DWH	1:10	25.5	96 h	EC_{50}	41.8 μg/L	CEWAF	Gov't & Res.			x		
Vignier et al.	2016	Lab	Acute	Oyster - 7-day	saline, expressed as oil	Corexit 9500	DWH	1:10	25.5	96 h	EC_{50}	72 μg/L	CEWAF	Gov't & Res.			x		
Vignier et al.	2016	Lab	Acute	Oyster - 14-day	saline, expressed as oil	Corexit 9500	DWH	1:10	25.5	96 h	EC_{50}	88 μg/L	CEWAF	Gov't & Res.			x		
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 1-day	saline, oil only	Oil only	DWH	1:10	25.5	96 h	EC_{20}	106 μg/L	HEWAF	Gov't & Res.					
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 7-day	saline, oil only	Oil only	DWH	1:10	25.5	96 h	EC_{20}	61 μg/L	HEWAF	Gov't & Res.					
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 14-day	saline, oil only	Oil only	DWH	1:10	25.5	96 h	EC_{20}	1.7 μg/L	HEWAF	Gov't & Res.					
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 1-day	saline, expressed as dispersa	Corexit 9500	DWH	1:10	25.5	96 h	EC_{20}	25 μg/L	CEWAF	Gov't & Res.		x			
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 7-day	saline, expressed as dispersa	Corexit 9500	DWH	1:10	25.5	96 h	EC_{20}	37 μg/L	CEWAF	Gov't & Res.		x			
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 14-day	saline, expressed as dispersa	Corexit 9500	DWH	1:10	25.5	96 h	EC_{20}	10.6 μg/L	CEWAF	Gov't & Res.		x			
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 1-day	saline, expressed as oil	Corexit 9500	DWH	1:10	25.5	96 h	EC_{20}	1.1 μg/L	CEWAF	Gov't & Res.		x			
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 7-day	saline, expressed as oil	Corexit 9500	DWH	1:10	25.5	96 h	EC_{20}	8.6 μg/L	CEWAF	Gov't & Res.		x			
Vignier et al.	2016	Lab	Sub-Lethal Effects	Oyster - 14-day	saline, expressed as oil	Corexit 9500	DWH	1:10	25.5	96 h	EC_{20}	35 μg/L	CEWAF	Gov't & Res.		x			

Adeyemo et al. (2015) studied the effects of the exposure of Menidia beryllina embryos at 30-48 hours post-fertilization to the water accommodated fractions of Macondo oil (WAF, 200 ppm, v/v), dispersants (20 ppm, v/v, Corexit 9500 or 9527), and mixtures of oil and each of the dispersants to produce chemically enhanced water accommodated fractions (CEWAFs) over a 72-hour period. The polyaromatic hydrocarbon (PAH) and benzene, toluene, ethylene and xylene (BTEX) constituents of the 5X concentrated exposure solutions (control, WAF, dispersants and CEWAFs) were determined and those of the 1× exposures were derived using a dilution factor. PAH, BTEX and low molecular weight PAH constituents greater than 1 ppb were observed in WAF and the dispersants, but at much higher levels in CEWAFs. The WAF and CEWAFs post-weathering were diluted at 1:5 (200 ml WAF/CEWAF: 800 ml 25 ppt saltwater) for embryo exposures. Mortality, heartbeat, embryo normalcy, abnormality types and severities were recorded. The qPCR assay was used to quantify abundances of transcripts of target genes for sexual differentiation and sex determination, growth regulation and stress response; and gapdh served as the housekeeping gene. Temperature was 21. °C throughout the experimental period, while mortality was low and not significantly different among treatments. Heartbeat was significantly different with the lowest heartbeats recorded in Corexit 9500 and 9527 exposed embryos compared with controls. Significantly more treated embryos were in a state of deterioration, with significantly more embryos presenting arrested tissue differentiation compared with controls. Exposure to WAF, dispersants and CEWAF induced aberrant expression of all the genes, with star, dmrt-1, ghr and hsp90 being significantly down-regulated in CEWAF and cyp19b in Corexit 9527. The cyp1a and cyp19b were significantly up-regulated in CEWAFs and WAF, respectively. The molecular endpoints were most sensitive, especially the expression of star, cyp19b, cyp1a, hsp90 and could therefore be used as early indicators of long term effects of Corexit 9500 and 9527 uses in oil spill management on M. beryllina.

Alexander et al. (2016) studied larval development toxicity tests using 3 life history stages of the Antarctic sea urchin (*Sterechinus neumayeri*) to assess the toxicity of physically dispersed, chemically dispersed, and dispersant-only water-accommodated fractions (WAFs) of an intermediate fuel oil (IFO 180, BP) and the chemical dispersant Slickgone NS (Dasic International). Despite much lower total petroleum hydrocarbon concentrations, physically dispersed fuels contained higher proportions of low-to-intermediate weight carbon compounds and were generally at least an order of magnitude more toxic than chemically-dispersed fuels. Based on concentrations that caused 50% abnormality (EC_{50}) values, the embryonic unhatched blastula life stage was the least affected by fuels and dispersants, whereas the larval 4-armed pluteus stage was the most sensitive. The results indicate that the use of a fuel dispersant did not increase the hydrocarbon toxicity of IFO 180 to the early life stages of Antarctic sea urchins, relative to physical dispersal.

Alloy et al. (2016) studied photoinduced toxicity following co-exposure to ultraviolet (UV) radiation and oil on Mahi-mahi (*Coryphaena hippurus*) embryos, which have positively buoyant, transparent eggs. These characteristics may result in mahi-mahi embryos being at particular risk from photoinduced toxicity. The goal of this study was to determine whether exposure to ultraviolet radiation as natural sunlight enhances the toxicity of crude oil to embryonic mahi-mahi. Mahi-mahi embryos were exposed to several dilutions of water accommodated fractions (WAF) from slick oil collected during the 2010 spill and gradations of natural sunlight in a fully factorial design. Dispersant may have been present but was not measured. Co-exposure to natural sunlight and WAF significantly reduced percent hatch in mahi-mahi embryos. Effect concentrations of PAH in WAF were within the range of surface PAH concentrations reported in the Gulf of Mexico during the Deepwater Horizon spill.

Almeda et al. (2014) determined the effects of Light Louisiana Sweet crude oil, dispersant Corexit 9500A, and dispersant-treated crude oil on the survival and growth rates of nauplii of the barnacle, Amphibalanus improvisus and tornaria larvae of the enteropneust Schizocardium sp. Growth rates of barnacle nauplii and tornaria larvae were significantly reduced after exposure to chemically dispersed crude oil and dispersant Corexit 9500A at concentrations commonly found in the water column after dispersant application. They also found that barnacle nauplii ingested dispersed crude oil, which may have important consequences for the biotransfer of petroleum hydrocarbons through coastal pelagic food webs after a spill. Application of chemical dispersants increases the impact of crude oil spills on meroplanktonic larvae.

Bejarano et al. (2015) carried out a quantitative review to evaluate the use of standard toxicity testing data to help inform decisions regarding dispersant use, recognizing some key issues with current practices, specifically, reporting toxicity metrics (nominal vs measured), exposure duration (standard durations vs short-term exposures), and exposure concentrations (constant vs spiked). Analytical chemistry data were used to demonstrate the role of oil loading on acute toxicity and the influence of dispersants on chemical partitioning. The analyses presented here suggest that decisions should be made on the basis of measured aqueous exposure concentrations and preferably, using data from short-term exposure durations under spiked exposure concentrations.

Bhattacharya et al. (2016) studied the in vitro cytotoxic effects of the chemicals trapped in tarmat fragments using hippocampal (neuron), kidney (nephron) and epithelial cells. Water accommodated fraction (WAF) of tarmat fragments was used in this study. Cytotoxicity was elucidated by the MTT assay and cellular morphology assessment. Markers of oxidative stress and apoptosis were assessed to study the toxicity effects. Tarmat WAF induced dose-dependent cellular toxicity. Chemicals trapped in tarmat WAF inhibited cell viability in the hippocampal, kidney and epithelial cells. Tarmat WAF also generated reactive oxygen species and increased activity of superoxide dismutase in hippocampal cells.

Dasgupta et al. (2015) evaluated the effects of short term (48 hr) exposures to Corexit EC9500A, water accommodated fractions (WAF), and chemically enhanced water accommodated fractions (CEWAF) prepared from Southern Louisiana Sweet Crude Oil (MC 242) on survival of sheepshead minnow (*Cyprinodon variegatus*) larvae held under normoxic (ambient air) or hypoxic (2 mg/L O_2) conditions. Results demonstrated that hypoxia significantly enhances mortality observed in response to Corexit or CEWAF solutions. In the latter case, significant interactions between the two stressors were also observed. The data supports the need to further evaluate the combined stresses imparted by hypoxia and exposure to petroleum hydrocarbons and dispersants.

DeLeo et al. (2016) examined the effects of bulk oil-water mixtures, water-accommodated oil fractions, the dispersant Corexit 9500A, and the combination of hydrocarbons and dispersants on three species of corals living near the spill site in the Gulf of Mexico between 500 and 1100 m depths: Paramuricea type B3, Callogorgia delta and Leiopathes glaberrima. Following short-term toxicological assays (0-96 h), all three coral species examined showed more severe health declines in response to dispersant alone (2.3-3.4 fold) and the oil-dispersant mixtures (1.1-4.4 fold) than in the oil-only treatments. Higher concentrations of dispersant alone and the oil-dispersant mixtures resulted in more severe health declines. C. delta exhibited somewhat less severe health declines than the other two species in response to oil and oil/dispersant mixture treatments, likely related to its increased abundance near natural hydrocarbon seeps. These experiments provide direct evidence for the toxicity of both oil and dispersant on deep-water corals.

Demopoulis et al. (2016) collected sediments adjacent to several coral habitats located 6 to 183 km from the wellhead in order to quantify the extent of impact of the DWH spill on infaunal communities. Higher variance in macrofaunal abundance and diversity, and different community structure (higher multivariate dispersion) were associated with elevated hydrocarbon concentrations and contaminants at sites closest to the wellhead, consistent with impacts from the spill. In contrast, variance in meiofaunal diversity was not significantly related to distance from the wellhead and no other community metric (e.g. density or multivariate dispersion) was correlated with contaminants or hydrocarbon concentrations. Concentrations of polycyclic aromatic hydrocarbons (PAH) provided the best statistical explanation for observed macrofaunal community structure, while depth and presence of fine-grained mud best explained meiofaunal community patterns. Impacts associated with contaminants from the DWH spill resulted in a patchwork pattern of infaunal community composition, diversity, and abundance, highlighting the role of variability as an indicator of disturbance.

Dussauze et al. (2014) compared the impact on tissue respiration of a dispersed oil (weathered Arabian Light) on two fish species, sea bass (*Dicentrarchus labrax*) and polar cod (*Boreogadus saida*) representative respectively of temperate and Arctic water ecosystems. Polar cod and sea bass were exposed for 48 hours to one of the following treatments: control, mechanically dispersed oil. chemically dispersed oil and dispersant alone. The impacts of these exposure conditions were assessed by heart energy metabolism using respirometry on permeabilized cardiac fibers. Following exposure, alteration in measurements of O_2 consumption by permeabilized cardiac fibers was found for the two species. The results show that for polar cod, oil alone decreased the activity of the respiratory chain whereas the dispersant alone did not have any impact. For sea bass, the results were different, dispersant alone decreased the activity of the respiratory chain whereas the results for oil alone were not different from the control group. These results show that oil and dispersants can alter mitochondrial activity.

Dussauze et el. (2015a) exposed juvenile sea bass for 48 h to dispersed oil (mechanically and chemically) or dispersants alone. The impact of these exposure conditions was assessed using growth and immunity. The increase observed in polycyclic aromatic hydrocarbon metabolites in bile indicated oil contamination in the fish exposed to chemical and mechanical dispersion of oil without any significant difference between these two groups. After 28 days of exposure, no significant differences were observed in specific growth rate, apparent food conversion efficiency and daily feeding). Following the oil exposure, fish immunity was assessed by a challenge with Viral Nervous Necrosis Virus (VNNV). Fish mortality was observed over a 42-day period. After 12 days post-infection, cumulative mortality was significantly different between the control group (16% $p \leq 0.05$) and the group exposed to chemical dispersion of oil (30% $p \leq 0.05$). However, at the end of the experiment, no significant difference was recorded in cumulative mortality or in VNNV antibodies secreted in fish in responses to the treatments. These data suggested that in the experimental condition, following the oil exposure, sea bass growth was not affected whereas an impact on immunity was observed during the first days. However, this effect on the immune system did not persist over time.

Dussauze et al. (2015b) evaluated effects of chemically dispersed oil by the dispersant Corexit 9500 on innate immunity and redox defenses in sea bass (*Dicentrarchus labrax*). The fish were exposed 48 h to four experimental conditions: a control group, a group only exposed to the dispersant (3.6. mg/L) and two groups exposed to 80 mg/L oil mechanically or chemically dispersed. Alternative pathway of complement activity and lysozyme concentration was measured in plasma in order to evaluate the general fish health status. Total glutathione, glutathione peroxidase (GPX) and superoxide dismutase (SOD) were analyzed in gills, liver, brain, intestine and muscle. The chemical dispersion induced a significant reduction of lysozyme concentration when compared to the controls, and the hemolytic activity of the alternative complement pathway was increased in mechanical and chemical dispersion. The analysis of SOD, GPX and total glutathione showed that antioxidant defenses were activated in liver and reduced in intestine and brain. Dispersant was also responsible for an SOD activity inhibition in these two last tissues, demonstrating a direct effect of this dispersant on reactive oxygen species homeostasis that can be interpreted as a signal of tissue toxicity. This result raised concerns about the use of dispersants and show that they can lead to adverse effects on marine species.

Dussauze et al. (2015c) assessed the relative acute toxicities of mechanically and chemically dispersed oil (crude Arabian Light) in controlled conditions. Juvenile sea bass (Dicentrarchus labrax) were exposed to 4 commercial formulations of dispersants (Corexit EC9500A, Dasic Slickgone NS, Finasol OSR 52, Inipol IP 90), to mechanically dispersed oil, and to the corresponding chemical dispersions. Acute toxicity was evaluated at 24 h, 48 h, 72 h, and 96 h through the determination of 10%, 50%, and 90% lethal concentrations calculated from measured total petroleum hydrocarbon (TPH) concentrations; Kaplan-Meyer mortality analyses were based on nominal concentrations. Fish were exposed to the dissolved fraction of the oil and to the oil droplets (ranging from 14.0 μm to 42.3 μm for the chemical dispersions). Kaplan-Meyer analyses demonstrated an increased mortality in the case of chemical dispersions. This difference can be attributed mainly to differences in TPH, because the chemical lethal concentrations were not reduced compared with mechanical lethal concentrations (except after 24 h of exposure). The ratios of lethal concentrations of mechanical dispersions to the different chemical dispersions were calculated to allow direct comparisons of the relative toxicities of the dispersions. The results ranged from 0.27 to 3.59 (mechanical to chemical), with a mean ratio close to 1 (0.92). These results demonstrate an absence of synergistic effect between oil and chemical dispersants.

Dussauze et al. (2016) evaluated pressure challenge as an assessment of consequences of chemically dispersed oil, followed by a high hydrostatic pressure challenge. This work was conducted on juvenile Seabass, *Dicentrarchus labrax*. Seabass were exposed for 48 h to dispersant alone (nominal concentration (NC) = 4 mg L^{-1}), mechanically dispersed oil (NC = 80 mg L^{-1}), two chemically dispersed types of oil (NC = 50 and 80 mg L^{-1} with a dispersant/oil ratio of 1/20), or kept in clean seawater. Fish were then exposed for 30 min at a simulated depth of 1350 m, corresponding to pressure of 136 absolute atmospheres (ATA). The probability of fish exhibiting normal activity after the pressure challenge significantly increased from 0.40 to 0.55 when they were exposed to the dispersant but decreased to 0.26 and 0.11 in the case of chemical dispersion of oil (at 50 and 80 mg L⁻1, respectively). The chemical dispersion at 80 mg L^{-1} also induced an increase in probability of death after the pressure challenge (from 0.08 to 0.26). This study clearly demonstrates the ability of a pressure challenge test to show the effects of a contaminant on the capacity of fish to face hydrostatic pressure.

Echols et al. (2015) evaluated waters from the Deepwater Horizon MC-252 incident for toxicity using *Americamysis bahia*, *Menidia beryllina* and *Vibrio fischeri* (Microtox assay). Organisms were exposed to GOM water samples collected in May-December 2010. Samples were collected where oil was visibly present on the water surface or the presence of hydrocarbons at depth was indicated by fluorescence data or reduced dissolved oxygen. Toxicity tests were conducted using water-accommodated fractions (WAFs), and oil-in-water dispersions (OWDs) (whole samples collected without dilution). Water samples collected from May to June 2010 were used for screening tests, with OWD samples slightly more acutely toxic than WAFs. Water samples collected in July through December 2010 were subjected to definitive acute testing with both species. In A. bahia tests, total PAH concentrations for OWD exposures ranged from non-detect to 23.0 μgL^{-1}, while WAF exposures ranged from non-detect to 1.88 μgL^{-1}. Mortality was > 20% in five OWD exposures with A. bahia and three of the WAF definitive tests. Total PAH concentrations were lower for M. beryllina tests, ranging from non-detect to 0.64 μgL-1 and non-detect to 0.17 μgL^{-1} for OWD and WAF exposures, respectively. Only tests from two water samples in both the WAFs and OWDs exhibited >20% mortality to M. beryllina. Microtox assays showed stimulatory and inhibitory responses with no relationship with PAH exposure concentrations. Most mortality in A. bahia and M. beryllina occurred in water samples collected before the well was capped in July 2010 with a clear decline in mortality associated with a decline in total PAH water concentrations.

Echols et al. (2016) evaluated ephyrae of the scyphozoan jellyfish, Aurelia aurita, in 96-hr acute toxicity tests for lethal response to Macondo crude oils from the Deepwater Horizon (DWH) incident in the Gulf of Mexico (GOM), Corexit 9500, and oil-dispersant mixtures. Water accommodated fractions (WAFs) of weathered and un-weathered Macondo crude oils were not acutely toxic to ephyrae (LC_{50}s > 100% WAF). The total PAHs (TPAHs), measured as the sum of 46 PAHs, averaged 21.1 and 152 μg TPAH/L for WAFs of weathered and un-weathered oil, respectively. Mortality was significantly higher in the three highest exposure concentrations (184-736 μg TPAH/L) of chemically dispersed WAFs (CEWAF) compared to controls. Dispersant only tests resulted in a mean LC_{50} of 32.3 μL/L, which is in the range of previously published LC_{50}s for marine zooplankton. Changes in appearance and muscle contractions were observed in organisms exposed to CEWAF dilutions of 12.5 and 25%, as early as 24 h post-exposure. Based on the results of these tests, crude oil alone did not cause significant acute toxicity; however, the presence of chemical dispersant resulted in substantial mortality and physical and behavioral abnormalities either due to an increase in hydrocarbons or droplet exposure.

Elarbaoui et al. (2015) investigated the effects of the use of chemical dispersants on meiobenthic organisms and nematodes in a mesocosm experiment. A 20-day experiment was performed in four experimental sets of mesocosms. In three of them, sediments were contaminated, respectively by oil (500 mg kg^{-1}), dispersed oil (oil + 5% dispersant), and dispersant alone, whereas in the last set sediments were kept undisturbed and used as a reference. The results showed that the meiobenthic response to oil contamination was rapid, for copepods and nematodes. One-way ANOVA showed a significant decrease of the abundance of copepods. In the case of nematodes, univariate and multivariate analyses indicated a clear decrease of the abundance of the species after only 20 days of pollutant exposure. In contrast, *Sphaerolaimus gracilis* and Sabateria sp. became more frequent within disturbed assemblages and appeared to be resistant and/or opportunistic species in the presence of these kinds of toxicants. Moreover, responses of copepods and nematodes to the treatment seemed to be the same irrespective of whether only oil or oil + dispersant was performed. The main toxicities of dispersed oil appear to be a result of increased quantities of increased dispersed oil droplets.

Esbaugh et al. (2016) developed a mahi-mahi spawning program to assess the effect of embryonic exposure to DWH crude oil with particular emphasis on the effects of weathering and dispersant on the magnitude of toxicity. Acute lethality (96 h LC_{50}) ranged from 45.8 μg/L ∑PAH for wellhead oil to 8.8 μg/L ∑PAH for samples collected from the surface slick, reinforcing previous work that weathered oil is more toxic on a ∑PAH basis. Differences in toxicity appear related to the amount of dissolved 3 ringed PAHs. The dispersant Corexit 9500 did not influence acute lethality of oil preparations. Embryonic oil exposure resulted in cardiotoxicity after 48 h, as evident from pericardial edema and reduced atrial contractility. Whereas pericardial edema appeared to correlate well with acute lethality at 96 h, atrial contractility did not. However, sub-lethal cardiotoxicity may impact long-term performance and survival. Dispersant did not affect the occurrence of pericardial edema; however, there was an apparent reduction in atrial contractility at 48 h of exposure. Pericardial edema at 48 h and lethality at 96 h were equally sensitive endpoints in mahi-mahi.

Frantzen et al. (2015) assessed concentration dependent differences in acute and long-term effects of a 48-h exposure to mechanically or chemically dispersed crude oil on juvenile lumpsucker (*Cyclopterus lumpus*). Acute or post-exposure mortality was only observed at oil concentrations representing higher concentrations than reported after real oil spills. Acute mortality was more apparent in chemically than mechanically dispersed oil treatments whereas comparable EC_{50}s were observed for narcosis. There was a positive correlation between EROD activity and muscle PAH concentration for the lower oil concentrations whereas higher concentrations inhibited the enzyme activity. The incidence of gill tissue lesions was low with no difference between dispersion methods or oil concentrations. A concentration dependent decrease in swimming- and feeding behavior and in SGR (Specific growth rate) was observed at the start of the post-exposure period, but with no differences between corresponding oil treatments. Three weeks post-exposure, fish from all treatments showed as high SGR as the control fish.

Frantzen et al. (2015) assessed concentration dependent differences in acute responses and long-term effects of a 48-h acute exposure to dispersed oil, with and without the application of a chemical dispersant, on the Arctic filter feeding bivalve *Chlamys islandica*. Icelandic scallops were exposed for 48 h to a range of spiked concentrations of mechanically and chemically dispersed oil. Short-term effects were assessed in terms of lysosomal membrane stability, superoxide dismutase, catalase, gluthatione S-transferases, glutathione peroxidases, glutathione reductase, glutathione, total oxyradical scavenging capacity, lipid peroxidation and peroxisomal proliferation. Post-exposure survival, growth and reproductive investment were followed for 2 months to evaluate any long-term consequence. Generally, similar effects were observed in scallops exposed to mechanically and chemically dispersed oil. Limited short-term effects were observed after 48 h, suggesting that a different timing would be required for measuring the possible onset of such effects. There was a concentration dependent increase in cumulative post-exposure mortality, but long-term effects on gonadosomatic index, somatic growth/condition factor did not differ among treatments.

Hansen et al. (2017) studied the contribution of mechanically-produced oil micro-droplet toxicity in dispersions by comparing exposures to oil dispersions (water soluble fraction with droplets) to concurrent exposure to filtered dispersions (water-soluble fractions without droplets). Physical (coloration) and behavioral (feeding activity) as well as molecular (metabolite profiling) responses to oil exposures in the copepod Calanus finmarchicus were studied. At high dispersion concentrations (4.1–5.6 mg oil/L), copepods displayed carapace discoloration and reduced swimming activity. Reduced feeding activity, measured as algae uptake, gut filling and fecal pellet production, was evident also for lower concentrations (0.08 mg oil/L). Alterations in metabolic profiles were also observed following exposure to oil dispersions. The pattern of responses was similar between two comparable experiments with different oil types, suggesting responses to be non-oil type specific. Furthermore, oil micro-droplets appear to contribute to some of the observed effects triggering a starvation-type response, manifested as a reduction in metabolite (homarine, acetylcholine, creatine and lactate) concentrations in copepods. The work clearly displays a relationship between crude oil micro-droplet exposure and reduced uptake of algae in copepods.

Laramore et al. (2014) conducted a series of acute and sub-lethal experiments to examine the potential effects of exposure to water-accommodated fractions (WAFs) of Macondo Canyon 252 crude oil and chemically-enhanced (Corexit 9500A dispersant) water-accommodated fractions (CEWAFs) on embryogenesis, larval development, growth, and survival of the eastern oyster, *Crassostrea virginica*. Nominal exposure concentrations for acute experiments were 0, 100, 200, 400, 800 and 1,200 mg/L for WAFs, and 0, 6.25, 12.5, 25, 50, 100, and 200 mg/L for CEWAFs. Calculated total polycyclic aromatic hydrocarbon (TPAH) values were 0, 22.5, 45, 90, 181, and 271 µg/L for WAFs, and 0, 4.5, 8.9, 17.8, 35.7, 71, and 142 µg/L for CEWAFs. The exposure concentration for sub-lethal experiments was 16 mg/L CEWAF. Total polycyclic aromatic hydrocarbon concentrations represent moderate to high levels of TPAH reported during the Deepwater Horizon (DWH) event. Exposure to acute concentrations of 1 or both of these contaminants was shown to decrease fertilization success (≥100 mg/L CEWAF), hinder trochophore (≥100 mg/L WAF, ≥12.5 mg/L CEWAF) and D-stage (≥200 mg/L WAF, ≥25 mg/L CEWAF) development, increase the risk of D-stage developmental abnormalities (≥100 mg/L WAF, ≥100 mg/L CEWAF), and decrease survival of D-stage (1,092 to 261.8 mg/L WAF, 24-96 h LC50; 177.6 to 24.8 mg/L CEWAF, 24-96 h LC50) and eyed (81.9 to 14.5 mg/L CEWAF; 24-96 h LC50) larvae. Exposure to CEWAFs, in general, resulted in increased toxicity over WAFs, likely as a result of the increased bioavailability of hydrocarbons. In contrast to acute exposures, short-term (24-h) sub-lethal exposure of D-stage larvae to CEWAFs (16 mg/L) had no impact on survival or growth. Concentrations used represent possible TPAH exposure levels based on maximum reported values.

Mauduit et al. (2016) developed a methodology to evaluate a fish's capacity to deal with an exposure to chemically dispersed oil, and characterize the long-term effects. They applied high-throughput, non-lethal challenge tests to assess hypoxia tolerance, temperature susceptibility and maximal swimming speed as proxies for a fish's functional integrity. These whole animal challenge tests were implemented before (1 month) and after (1 month) juvenile European sea bass (Dicentrarchus labrax) had been acutely exposed (48 h) to a mixture containing 0.08 g/L of weathered Arabian light crude oil plus 4% dispersant (Corexit EC9500A). In addition, experimental populations were then transferred into semi-natural tidal mesocosm ponds and correlates of Darwinian fitness (growth and survival) were monitored over a period of 4 months. Results revealed that fish acutely exposed to chemically dispersed oil remained impaired in terms of their hypoxia tolerance and swimming performance, but not in temperature susceptibility for 1-month post-exposure. These functional impairments had no subsequent ecological consequences under mildly selective environmental conditions since growth and survival were not impacted during the mesocosm pond study. Furthermore, the earlier effects on fish performance were presumably temporary because re-testing the fish 10 months post-exposure revealed no significant residual effects on hypoxia tolerance, temperature susceptibility and maximal swimming speed.

Mearns et al. (2014, 2015, 2016) review articles on pollution effects on the environment including that of oil and petroleum.

Michaelson et al. (2015) studied fluctuating asymmetry (small, non-random deviations from perfect bilateral symmetry) which is an informative metric sensitive to contaminants that can be used to assess environmental stress levels. For this study, the well-studied and common Gulf of Mexico estuarine fish, *Menidia beryllina*, was used with pre- and post-oil spill collections. Comparisons of fluctuating asymmetry in three traits (eye diameter, pectoral fin length, and pelvic fin length) were made pre- and post-oil spill across two sites (Old Fort Bayou and the Pascagoula River), as well as between years of collection (2011, 2012)-one and two years, respectfully, after the spill in 2010. They hypothesized that fluctuating asymmetry would be higher in post-Deepwater Horizon samples, and that this will be replicated in both study areas along the Mississippi Gulf coast. They also predicted that fluctuating asymmetry would decrease through time after the oil spill as the oil weathered or was removed. Analyses performed on 1135 fish (220 pre- and 915 post Deepwater Horizon) showed significantly higher post spill fluctuating asymmetry in the eye but no difference for the pectoral or pelvic fins. There was also higher fluctuating asymmetry in one of the two sites both pre- and post-spill, indicating observed asymmetry may be the product of multiple stressors. Fluctuating asymmetry decreased in 2012 compared to 2011. Fluctuating asymmetry is a sensitive measure of sub lethal stress, and the observed variability in this study (pre- vs. post-spill or between sites) could be due to a combination of oil, dispersants, or other unknown stressors.

Mu et al. (2014) assessed the bioavailability and chronic toxicity of water-accommodated fractions of crude oil (WAFs) and 2 dispersants plus dispersed crude oil (chemical dispersant+crude oil [CE-WAF] and biological dispersant+crude oil [BE-WAF]) on the early life stages of marine medaka, *Oryzias melastigma*. The results showed that the addition of the 2 dispersants caused a 3- and 4-fold increase in concentrations of total priority polycyclic aromatic hydrocarbons (PAHs) and high-molecular-weight PAHs with 3 or more benzene rings. The chemical and biological dispersants increased the bioavailability (as measured by ethoxyresorufin-O-dethylase activity) of crude oil 6-fold and 3-fold, respectively. Based on nominal concentrations, chronic toxicity (as measured by deformity) in WAFs exhibited a 10-fold increase in CE-WAF and a 3-fold increase in BE-WAF, respectively. When total petroleum hydrocarbon was measured, the differences between WAF and CE-WAF treatments disappeared, and CE-WAF was approximately 10 times more toxic than BE-WAF. Compared with the chemical dispersant, the biological dispersant possibly modified the toxicity of oil hydrocarbons because of the increase in the proportion of 2- and 3-ringed PAHs in water. The chemical and biological dispersants enhanced short-term bioaccumulation and toxicity, through different mechanisms.

Muncaster et al. (2016) exposed yellowtail kingfish (YTK), *Seriola lalandi*, embryos in static incubations to the water-accommodated fraction (WAF) of Rena heavy fuel oil as well as a similar preparation treated with the commercial dispersant Corexit 9500. Mortality in WAF treatments generally increased in association with total polycyclic aromatic hydrocarbon (tPAH) concentration over a 24-h period. Physical abnormalities were observed in some of the larvae exposed to WAF for 48 h. There was no survival in dispersed oil treatments after 24 h of exposure. These treatments had greater tPAH concentrations (2–53 μgL^{-1}) than equivalent WAF dilutions (0.2–1.5 μgL^{-1} tPAH). Indications are that significant morbidity is induced in YTK at ecologically relevant tPAH concentrations.

Nordtug et al. (2015) investigated the rates of ingestion of oil microdroplets and oil fouling in the zooplankton filter-feeder (*Calanus finmarchicus* at 3 concentrations of oil dispersions ranging from 0.25 mg/L to 5.6 mg/L. To compare responses to mechanically and chemically dispersed oil, the copepods were exposed to comparable dispersions of micron-sized oil droplets made with and without the use of a chemical dispersant (similar oil droplet size range and oil concentrations) together with a constant supply of microalgae for a period of 4 d. The filtration rates as well as accumulation of oil droplets decreased with increasing exposure concentration. The estimated total amount of oil associated with the copepod biomass for the two lowest exposures in the range 11 mL/kg to 17 mL/kg, was significantly higher than the approximately 6 mL/kg found in the highest exposure. For the two lowest concentrations, the filtration rates were significantly higher in the presence of chemical dispersant. Furthermore, a significant increase in the amount of accumulated oil in the presence of dispersant was observed in the low exposure group.

Nørregaard et al. (2015) caught resting high Arctic C. hyperboreus (copepods) in Disko Bay at >250 meters depth, November 2013, and subsequent experimental work was initiated immediately after, at nearby Arctic Station at Disko Island, Western Greenland. C. hyperboreus females were incubated in phenanthrene (111, 50 and 10 nM), pyrene (57, 28 and 6 nM) and benzo(a) pyrene (10, 5 and 1 nM) for three days in treatments with and without oil (corn oil) and dispersant (AGMA DR372). After exposure, the highest measured concentrations of respectively phenanthrene, pyrene and benzo(a) pyrene in the copepods were 129, 30 and 6 nmol PAH g /female. Results showed that with addition of oil and dispersant to the water, the accumulation of PAH was significantly reduced, due to the deposition of the PAHs in the oil phase, decreasing the available PAHs for copepod uptake. While PAH metabolites and a depuration of the PAHs were observed, the copepods still contained PAHs after 77 days of incubation in clean seawater. Differences of treatments with and without oil and dispersant on the egg production were not statistically conclusive, although it is the most likely an effect of the highly variable day-to-day egg production between individual copepods. Equally, although there was an indication that the addition of dispersant and oil increased the mortality rate, there was no statistical difference.

Nwaizuzu et al. (2015) reviewed literature on oil spill dispersants from 1994-2014 focusing on their toxicity and biodegradability. From the review, many researchers reported that dispersed oil is more toxic than the crude oil while very few were able to show that the dispersed oil was less toxic or equal in toxicity to the crude oil. They also showed that the dispersant increased the concentration of PAHs in the water column, this some attributed to be the cause of the increased toxicity. The effect of the toxicity on the various organs of the organism was noted as some recorded lesions on the gills of fish, drop in heart rate and so on. Many studies suggested that dispersants do actually increase the biodegradability although to some it was restricted to some components of the crude oil. Some researchers however showed that the dispersant reduced the biodegradability of the crude oil. Also noted was the fact that various crude oils reacted differently when mixed with a dispersant. Aquatic organisms reacted differently to different combinations of the dispersed oil. Temperature was shown to play a role in rate of biodegradability.

Nwaizuzu et al. (2016) investigated the toxicological effects of OSD Seacare and Bonny light crude oil on the African Catfish (*Clarias gariepinus*). The 96-hr acute toxicity of the water accommodated fraction (WAF) of the mixture of OSD Seacare and Bonny light crude oil was investigated as well as the critical body residue on the fingerlings of the African Catfish. The mean weight and height of the fish was 1.27 g and 5.35 cm respectively. The following concentrations, 30, 90, 180 and 270 ml/L, were used for the CEWAF test. The LC_{50} for the CEWAF was determined to be 199 ml/L while no death was recorded in the WAF test. The dispersant Seacare increased the toxicity of the crude oil on the test organism by more than 4.5 times further proving that oil spill dispersants can increase the toxicity of crude oil on aquatic organisms. There was no PAH recorded in the fish from the control. From the fish exposed to 30 ml/L of the dispersed oil concentration, the total PAH concentration was 0.73 ppm with 1 Benzo (g,h,i) perylene accounting for the total amount. Whereas the total PAH in the fish exposed to the 270 ml/L concentration was 2.5 ppm with Naphthalene accounting for the total amount. After the acute toxicity testing and the test organisms were put in clean water, it was noticed that the test organisms exposed to the dispersed oil had a change in color and there was reduced feeding in both those exposed to the WAF of the crude oil and dispersed oil.

Olsen et al. (2016) assessed the sensitivity of a macro-benthic deep-sea organism (*Eurythenes gryllus*) to determine the concentration causing lethality to 50 % of test individuals (LC_{50}) after an exposure to dispersed Arabian Light oil. The LC_{50} (24 h) was 101 and 24 mg/L after 72 h and 12 mg/L at 96 h. Based on the EPA scale of toxicity categories to aquatic organisms, an LC_{50} (96 h) of 12 mg/L indicates that the dispersed oil was slightly to moderately toxic to E. gryllus.

Overholt et al. (2016) utilized two environmentally relevant species of hydrocarbon-degrading bacteria to quantify the response to Macondo crude oil and Corexit 9500A-dispersed oil in terms of bacterial growth and oil degradation potential. In addition, specific hydrocarbon compounds were quantified in the dissolved phase of the medium and linked to ecotoxicity using a U.S. Environmental Protection Agency-approved rotifer assay. Bacterial treatment significantly and drastically reduced the toxicity associated with dispersed oil (increasing the 50% lethal concentration [LC_{50}] by 215%). The growth and crude oil degradation potential of Acinetobacter were inhibited by Corexit by 34% and 40%, respectively; conversely, Corexit significantly enhanced the growth of Alcanivorax by 10% relative to that in undispersed oil. Furthermore, both bacterial strains were shown to grow with Corexit as the sole carbon and energy source. Hydrocarbon-degrading bacterial species demonstrate a unique response to dispersed oil compared to their response to crude oil, with potentially opposing effects on toxicity. While some species have the potential to enhance the toxicity of crude oil by producing biosurfactants, the same bacteria may reduce the toxicity associated with dispersed oil through degradation or sequestration.

Peiffer and Cohen (2015) established the lethal levels for water-accommodated fractions of Corexit 9500A chemical dispersant, crude oil (WAF), and dispersed crude oil (CEWAF) for the ctenophore *Mnemiopsis leidyi* (comb jelly) at both 15 and 23°C. This gelatinous zooplankter was sensitive to dispersant at both temperatures, as well as to oil solutions, with some increase in toxicity of CEWAF as compared to WAF. Subsequent sublethal assays for routine respiration rate, bioluminescence, and glutathiones- transferase activity were conducted on individuals surviving 24 h exposures to test solutions at both 15 and 23°C. GST activity increased significantly in 2.5 and 5 mg/L dispersant solutions at 15°C, suggesting a metabolic detoxification response to the dispersant-containing solutions, but no effect of any solution type on routine respiration rate was observed. Light emission through mechanically stimulated bioluminescence and photocyte lysis decreased with exposure to crude oil WAF and CEWAF at both temperatures and to dispersant exposure at 23°C. Collectively, these results demonstrate that M. leidyi exhibits both lethal and sublethal effects from acute crude oil exposure, with an elevation of some sublethal responses upon addition of chemical dispersant. Sublethal effects of oil and dispersants in pelagic species, most notably impairment of luminescence, should be considered in dispersion.

Redman et al. (2017) carried out toxicity tests to improve the understanding of the role of droplets, using acute toxicity tests with *Daphnia magna* and *Americamysis bahia* with Endicott crude oil in low-energy mixing systems with and without Corexit 9500 dispersant. Exposures were also prepared by placing crude oil in silicone tubing and passively dosing test media to provide dissolved oil exposures without droplets. A framework was described for characterizing dissolved phase exposures using both mechanistic modeling and passive sampling measurements. The approach is then illustrated by application to data from the present study. Expression of toxicity in terms of toxic units calculated from modeled dissolved oil concentrations or passive sampling measurements showed similar dose responses between exposure systems and organisms, despite the gradient in droplet oil. These results indicate that droplets do not appreciably contribute to toxicity for the two species investigated.

Santander-Avanceña (2016) assessed the toxicity of water-accommodated fraction (WAF) and chemically enhanced WAF (CEWAF) of bunker C oil and dispersant to a microalga, *Tetraselmis tetrathele*. The 72-h median effective concentration (72-h EC_{50}) of CEWAF and dispersant were determined at 3.30 % and 2.40 %, respectively. The no-observed effect concentration (NOEC) of CEWAF to T. tetrathele was at 2.0 % and lowest observed effect concentration (LOEC) was at 3.0 % while NOEC and LOEC of the dispersant to T. tetrathele were determined at 1.0 % and 2.0 %, respectively. The addition of dispersant to oil increased the amount of total PAH present in the CEWAF test solutions. Dispersant alone was highly toxic, and the toxicity of CEWAF was primarily caused by the presence of dispersant.

Tissier et al. (2015) assessed the impact of dispersed oil in *Dicentrarchus labrax*, a fish frequently used as an oil contamination indicator species. Fish were exposed for 48 h to (mechanically and chemically) dispersed oil and dispersant alone. The impact of these exposure conditions was assessed on cardiac function by measuring (i) the contraction strength, the contraction and the relaxation speeds (ii) the cardiac energy metabolism using respirometry on permeabilized cardiac fibers. Compared to control, the increase of polycyclic aromatic metabolites observed in the bile indicated oil contamination in the specimen fish. Following 48 h of oil exposure at realistic oil concentrations, alterations of cardiac performances were observed. A decrease in contraction strength, contraction and relaxation speeds was observed in the presence of oil without effect of dispersant on these three parameters. Looking at cardiac energy metabolism, dispersant alone decreases all the activity of the respiratory chain and increases the proton leak. From these results, it appears that the observed decrease in cardiac performance in fish exposed to oil was not linked to a decrease in energy availability. This study demonstrated that dispersed crude oil has an impact on seabass cardiac contraction parameters and that the dispersant Finasol OSR 52 has an effect on maximal mitochondrial energy production and proton leak. Thus, the dispersant oil mixture could lead to a decrease of fish metabolic capacity.

Vignier et al. (2015) evaluated the effects of exposing gametes and embryos of C. virginica (oyster) to dispersant alone (Corexit), mechanically (HEWAF) and chemically dispersed (CEWAF) DWH oil. Fertilization success and the morphological development, growth, and survival of larvae were assessed. Gamete exposure reduced fertilization (HEWAF: EC_{20} 1 h = 1650 µg tPAH50 L^{-1}; CEWAF: EC_{20} 1 h = 19.4 µg tPAH50 L^{-1}; Corexit: EC_{20} 1 h = 6.9 mg L^{-1}). CEWAF and Corexit showed a similar toxicity on early life stages at equivalent nominal concentrations. Oysters exposed from gametes to CEWAF and Corexit experienced more deleterious effects than oysters exposed from embryos. Results suggest the presence of oil and dispersant during oyster spawning season may interfere with larval development and subsequent recruitment.

Vignier et al. (2016) studied the effects of oil and dispersant on planktonic larval stages of the oyster, C. virginica (veliger (1-day), umbo (10-day) and pediveliger (14-day)) were tested in the laboratory. Exposures to HEWAF, CEWAF and dispersant were toxic to larvae impairing growth, settlement success and ultimately survival. Larval growth and settlement were reduced at concentrations of oil ranging from 1.7 to 106 µg/L for HEWAF and 1.1–35 µg/L for CEWAF, concentrations well within the range of water sampled during the DWH oil spill. Sublethal effects induced by oil and dispersant could have significant ecological implications on oyster populations.

Vignier et al. (2017) evaluate the cellular effects of acute exposure of spermatozoa and oocytes to surface slick oil, dispersed mechanically (HEWAF) and chemically (CEWAF), using flow-cytometric (FCM) analyses, and (ii) determine whether the observed cellular effects relate to impairments of fertilization and embryogenesis of gametes exposed to the same concentrations of CEWAF and HEWAF. Following a 30-min exposure, the number of spermatozoa and their viability were reduced due to a physical action of oil droplets (HEWAF) and a toxic action of CEWAF respectively. Additionally, reactive oxygen species production in exposed oocytes tended to increase with increasing oil concentrations suggesting that exposure to dispersed oil resulted in an oxidative stress. The decrease in fertilization success (1-h), larval survival (24-h) and increase in abnormalities (6-h and 24-h) may be partly related to altered cellular characteristics. FCM assays are a good predictor of sublethal effects especially on fertilization success. These data suggest that oil/dispersant are cytotoxic to gametes, which may affect negatively the reproduction success and early development of oysters.

Volety et al. (2016) examined the impacts of chemically-enhanced water-accommodated fractions [CEWAF; 1.29-26.14 µg/l tPAH50 (a sum of 50 different polycyclic aromatic hydrocarbons)], high-energy water-accommodated fractions (HEWAF; 16.53-248.89 µg/l tPAH50), and dispersants (0.625-10 mg/l) on the cellular functions (viability, mitochondrial membrane potential (MMP), reactive oxygen species production (ROS), and acrosomal integrity) and resulting fertilization success of eastern oyster Crassostrea virginica spermatozoa. While viability of spermatozoa was not affected by CEWAF and HEWAF at concentrations tested, dispersant exposure caused significant decrease in viability at the highest concentration tested. Fertilization success as well as MMP and ROS production were significantly decreased upon exposure to CEWAF, HEWAF, and dispersants. Also, although not affected by HEWAF exposure, acrosomal integrity decreased upon exposure to CEWAF and dispersants at concentrations tested. The results of this study suggest that impaired fertilization and reduced viability observed after exposure to DWH oil spill contaminants may result, from alterations of cellular functions of spermatozoa and contribute to negative effects on oyster populations.

Yang and Xiong (2015) analyzed the hydrocarbon compositions of the mechanically dispersed water accommodated fraction (MDWAF) and the chemically dispersed water accommodated fraction (CDWAF) of No. 120 fuel oil, their bioaccumulation, and DNA damage related to oil exposure, using the sea urchin as a sentinel organism. The results show that the concentration of polycyclic aromatic hydrocarbon in the tissues of sea urchin exposed to the CDWAF is higher than that of those exposed to the MDWAF. The single cell gel electrophoresis assay results also indicated higher DNA damage from exposure to the CDWAF of oil. Thus, dispersants should be applied with caution in oil spill accidents.

Results from Previous Literature Reviews

2002 Older studies have generally shown that the acute toxicity to most species is the same for oil and dispersed oil at the same concentrations. Exceptions to this, where the dispersed oil has shown more toxicity, are reported in the literature and some examples were shown.

2008 Of the recent toxicity studies, most researchers (about 75 %) found that chemically-dispersed oil was more toxic than physically-dispersed oil. About half of these found that the cause for this was the increased PAHs (typically about 5 to 10 times) in the water column. Others noted the increased amount of total oil in the water column. Two researchers noted the damage to fish gills caused by the increased amounts of droplets. Less than 1/4 of researchers noted that chemically-dispersed oil was roughly equivalent to physically-dispersed oil.

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

2014 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.

3.2.2 Aquatic Toxicity of Dispersants Alone

Introduction

Some studies focussed on the inter-comparison of the aquatic toxicities of different dispersant products rather than the comparison of chemically-dispersed and mechanically-dispersed oil. This section focuses on that inter-dispersant comparison. The numeric results are summarized in Table 2. Some of the results from the previous section (dispersants with out) are included where when oil only was discussed.

Summary and Conclusions

The test results of dispersant toxicity alone are shown in Table 2. 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 specific dispersant, the species, life stage and the conditions of exposure and measurement,
b) Many of the more common dispersants such as Corexit 9500, Finasol OSR 52 and Dasic Slickgone NS have similar aquatic toxicities with the latter being generally lower.
c) The aquatic toxicities tanking by EPA would result in a rating of moderately toxic for Corexit 9500, and Finasol OSR 52.
d) The components of Corexit 9500 were studied separately and these studies show that the toxicity of the components are in line with the overall toxicity of the product.
e) In some studies, the dispersants were found to be somewhat cytotoxic and genotoxic.

g) Dispersants by themselves can cause damage to coral species at relatively low concentrations.

Detailed Study Summaries

DeLorenzo et al. (2016) examined the effects of salinity on the toxicity of two oil dispersants, Corexit 9500 and Finasol OSR 52. The grass shrimp, *Palaemonetes pugio*, was used as a test species. It is a euryhaline species that tolerates salinities from brackish to normal seawater. Adult and larval life stages were tested with each dispersant at three salinities, 5, 20, and 30 ppt. Median acute lethal toxicity thresholds and oxidative stress responses were determined. The toxicity of both dispersants was significantly influenced by salinity, with greatest toxicity observed at the lowest salinity tested. Larval shrimp were significantly more sensitive than adult shrimp to both dispersants, and both life stages were significantly more sensitive to Finasol than to Corexit (toxicities varied from 17 to 447 mg/L depending on salinity, life stage and dispersant). Oxidative stress in adult shrimp, as measured by increased lipid peroxidation activity, occurred with exposure to both dispersants.

Pie and Mitchelmore (2015) examined the acute toxicity of five oil spill chemical dispersants on the blue crab *Callinectes sapidus*. Static, non-renewal 48 h acute toxicity tests were performed on stage-II blue crab zoea. The median lethal concentration (LC_{50}) was calculated for each dispersant at 24 h and 48 h using nominal concentrations for each dispersant tested. The 48 h LC_{50} values from the most to the least toxic ranged from 10.1 mg/L for Dispersit SPC 1000 to 76.5 mg/L for Orca. For all dispersants, the swimming activity and mobility of larvae decreased with increasing dispersant concentration within 24 h of exposure and reached relative immobility at concentrations below LC_{50} values. These results show that the dispersants examined in this study are only slightly toxic after 48 h exposure to the earliest life stage of blue crabs that might likely be exposed to dispersants in the environment, with the exception of Dispersit SPC 1000 that bordered between slightly and moderately toxic. Although the dispersants themselves appear to not cause substantial acute toxicity, sublethal and potentially delayed impacts, such as, reduced mobility or food source availability could indirectly remove larvae from the population and need to be further examined, as do larval responses in standard chronic toxicity tests.

Studivan et al. (2015) studied dispersant exposure to corals. The aims of the study were: (1) to determine the extent of bleaching after acute 24 h and 72 h exposures of sublethal concentrations (0-50 ppm) of Corexit to the pulsing soft coral Xenia elongata and (2) to investigate a percent symbiont loss calculation using zooxanthellae density. The percent symbiont loss calculation was compared to a traditional metric of normalizing zooxanthellae density to soluble protein content. Percent symbiont loss was an effective measure of coral stress in acute Corexit exposures, while protein normalized zooxanthellae density was more variable. The bleaching data suggest a positive relationship between dispersant concentration and percent symbiont loss, culminating in excessive tissue necrosis and coral mortality within 72 h in high concentration exposures. Percent beaching ranged from 25% in 5 ppm exposures to 100% in 50 ppm exposures. Corexit also caused a significant decrease in pulse activity and relative oxygen saturation, possibly indicating a reduction in photosynthetic efficiency. This study and other similar research indicate that dispersant exposure is highly damaging to marine organisms, including ecologically important coral species.

Table 2 Toxicity Studies on Dispersant Alone

Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Temp °C	Time	Result	Value	Funder
Adams et al.	2014	Lab	Acute	Herring - juvenile	saline	Corexit 9500	10	24 d	LC_{50}	29.5 mg/L	Gov't & Res.
Almeda et al.	2014	Lab	Acute	Nauplii of Coral	saline	Corexit 9500	25	72 h	LC_{50}	.05 µL/L	Gov't & Res.
Almeda et al.	2014	Lab	Sub-Lethal Growth	Nauplii of Coral	saline	Corexit 9500	25	72 h	EC_{50}	.05 µL/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Larval Glass Shrimp	20 ppt salinity	Finasol OSR 52	25	96 h	LC_{50}	16.8 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Larval Glass Shrimp	20 ppt salinity	Corexit 9500	25	96 h	LC_{50}	40.1 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Larval Glass Shrimp	5 ppt salinity	Finasol OSR 52	25	96 h	LC_{50}	8.21 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Larval Glass Shrimp	30 ppt salinity	Finasol OSR 52	25	96 h	LC_{50}	29.4 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Larval Glass Shrimp	5 ppt salinity	Corexit 9500	25	96 h	LC_{50}	35.4 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Larval Glass Shrimp	30 ppt salinity	Corexit 9500	25	96 h	LC_{50}	67.6 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Adult Glass Shrimp	5 ppt salinity	Finasol OSR 52	25	96 h	LC_{50}	15.1 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Adult Glass Shrimp	20 ppt salinity	Finasol OSR 52	25	96 h	LC_{50}	32.3 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Adult Glass Shrimp	30 ppt salinity	Finasol OSR 52	25	96 h	LC_{50}	64.5 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Adult Glass Shrimp	5 ppt salinity	Corexit 9500	25	96 h	LC_{50}	377 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Adult Glass Shrimp	20 ppt salinity	Corexit 9500	25	96 h	LC_{50}	419 mg/L	Gov't & Res.
DeLorenzo et al.	2016	Lab	Acute	Adult Glass Shrimp	30 ppt salinity	Corexit 9500	25	96 h	LC_{50}	447 mg/L	Gov't & Res.
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Corexit 9500	16	24 h	LC_{50}	203.5 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Corexit 9500	16	48 h	LC_{50}	132.6 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Corexit 9500	16	72 h	LC_{50}	127.1 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Corexit 9500	16	96 h	LC_{50}	109.7 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Dasic Slickgone NS	16	24 h	LC_{50}	924.3 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Dasic Slickgone NS	16	48 h	LC_{50}	534.4 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Dasic Slickgone NS	16	72 h	LC_{50}	466.9 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Dasic Slickgone NS	16	96 h	LC_{50}	414.6 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Finasol OSR 52	16	24 h	LC_{50}	74.4 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Finasol OSR 52	16	48 h	LC_{50}	76.7 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Finasol OSR 52	16	72 h	LC_{50}	76.7 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Finasol OSR 52	16	96 h	LC_{50}	76.8 mg/L	Industry
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Inipol IP 90	16	72 h	LC_{50}	232.4mg/L	Industry

Table 2 Toxicity Studies on Dispersant Alone

Author(s)	Year	Type	Type of Test	Species	Conditions	Dispersant	Temp °C	Time	Result	Value	Funder
Dussauze et al.	2015c	Lab	Acute	Sea Bass juveniles	saline	Inipol IP 90	16	96 h	LC_{50}	189.5 mg/L	Industry
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Corexit 9500	22-23	24 h	LC_{50}	105.6 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Corexit 9500	22-23	48 h	LC_{50}	55 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Sub-Lethal -	Blue Crab Larvae	saline	Corexit 9500	22-23	Moribund	EC_{50}	75 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Dispersit SPC	22-23	24 h	LC_{50}	41 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Dispersit SPC	22-23	48 h	LC_{50}	10.1 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Sub-Lethal -	Blue Crab Larvae	saline	Dispersit SPC	22-23	Moribund	EC_{50}	10 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Orca	22-23	24 h	LC_{50}	169.7 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Orca	22-23	48 h	LC_{50}	76.5 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Sub-Lethal -	Blue Crab Larvae	saline	Orca	22-23	Moribund	EC_{50}	75 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Petro-Clean	22-23	24 h	LC_{50}	>100 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Petro-Clean	22-23	48 h	LC_{50}	52 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Sub-Lethal -	Blue Crab Larvae	saline	Petro-Clean	22-23	Moribund	EC_{50}	100 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Sea Brat #4	22-23	24 h	LC_{50}	105.2 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Acute	Blue Crab Larvae	saline	Sea Brat #4	22-23	48 h	LC_{50}	41 mg/L	Gov't & Res.
Pie & Mitchelmore	2015	Lab	Sub-Lethal -	Blue Crab Larvae	saline	Sea Brat #4	22-23	Moribund	EC_{50}	75 mg/L	Gov't & Res.
Studivan et al.	2016	Lab	Acute	Coral - *Xenia elongata*	Lethal and Bleaching	Corexit 9500	25	24 h	EC_{50}	28 ppm	Gov't & Res.
Studivan et al.	2016	Lab	Acute	Coral - *Xenia elongata*	Lethal and Bleaching	Corexit 9500	25	72 h	EC_{50}	25.5 ppm	Gov't & Res.
Toyota et al.	2016	Lab	Acute	Daphnia Magna	fresh	Corexit 9500	18	48 h	EC_{50}	1.31 ppm	Gov't & Res.
Toyota et al.	2016	Lab	Reproductive	Daphnia Magna	fresh	Corexit 9500	19	21 d	LOEC	4 ppm	Gov't & Res.
Toyota et al.	2016	Lab	Reproductive	Daphnia Magna	fresh	Corexit 9500	18	21 d	NOEC	2 ppm	Gov't & Res.
Vignier et al.	2016	Lab	Acute	Oyster - 1 day old	saline	Corexit 9500	25.6	96 h	LC_{50}	22.9 mg/L	Gov't & Res.
Vignier et al.	2016	Lab	Acute	Oyster - 7 day old	saline	Corexit 9500	25.6	96 h	LC_{50}	58 mg/L	Gov't & Res.
Word et al.	2016	Lab	Acute	Silverside - Menidia	saline	Corexit 9500a	25	96 h	LC_{50}	42.1 ppm	Industry
Word et al.	2016	Lab	Acute	Silverside - Menidia	saline	Corexit 9500b	25	96 h	LC_{50}	35.4 ppm	Industry
Word et al.	2016	Lab	Acute	Silverside - Menidia	saline	Cleaning product	25	96 h	LC_{50}	5.4-591 ppm	Industry
Word et al.	2016	Lab	Acute	Shrimp - A. bahia	saline	Corexit 9500a	25	96 h	LC_{50}	44.8 ppm	Industry
Word et al.	2016	Lab	Acute	Shrimp - A. bahia	saline	Corexit 9500b	25	96 h	LC_{50}	45.3 ppm	Industry
Word et al.	2016	Lab	Acute	Shrimp - A. bahia	saline	Cleaning product	25	96 h	LC_{50}	13-413 ppm	Industry

Toyota et al. (2017) used the cladoceran crustacean, water flea *Daphnia magna* a well-established model species for freshwater toxicological tests, including detection of juvenile hormone-like activity in test compounds. They conducted laboratory experiments to investigate the acute and chronic toxicity of Corexit 9500 using D. magna. The acute toxicity test was conducted according to OECD TG202 and the 48 h EC50 was 1.31 ppm. The reproductive chronic toxicity test was performed following OECD TG211 ANNEX 7 and 21 days LOEC and NOEC values were 4.0 and 2.0 ppm, respectively. These results indicate that Corexit 9500 has toxic effects on daphnids, particularly during the neonatal developmental stage, whereas juvenile hormone-like activity was not identified of Corexit 9500 on daphnids. The authors suggest that application of this type of chemical dispersant may have serious impacts on freshwater ecosystems by disrupting the key food chain network.

Vignier et al. (2016) studied the effects of dispersant on planktonic larval stages of the oyster, C. virginica (veliger (1-day), umbo (10-day) and pediveliger (14-day)) were tested in the laboratory. The toxicities of the dispersant alone were similar but lower (less toxic) than oil with dispersant, but much more toxic than oil alone.

Word et al. (2015) conducted laboratory tests by regulatory agencies to further evaluate and substantiate the existing aquatic toxicity of Corexit dispersants. To help put dispersant toxicity in context, two independent accredited labs were commissioned to conduct parallel studies that compared the acute toxicity of Corexit 9500 to common household cleaning agents. The results indicate that the acute toxicity of Corexit 9500 to marine aquatic organism is either within the median range or less toxic than the household cleaning agents tested. The median LC50 value for Corexit 9500 exposures to *Americamysis bahia* (shrimp-like crustacean native to Texan waters) was 42.5 mg/L (four products were less toxic and four products were more toxic); whereas, the median LC50 value for Corexit 9500 exposures to *Menidia beryllina* (inland Silverside) was 73.1 mg/L (one product was less toxic and seven products were more toxic).

Xi et al. (2016) noted that 2-Butoxyethanol and sorbitan monolaurate are major components of oil dispersants that are applied in large quantities to control oil spill in the aquatic environment. An important question is whether aquatic animals are equipped with mechanisms for the detoxification of these oil dispersant compounds. The current study aimed to examine whether zebrafish cytosolic sulfotransferases (SULTs) are capable of sulfating 2-butoxyethanol and sorbitan monolaurate. A systematic analysis of 18 zebrafish SULTs revealed that SULT3 ST1 showed the strongest sulfating activity toward 2-butoxyethanol, while SULT1 ST3 displayed the strongest sulfating activity toward sorbitan monolaurate. The pH-dependence of these two SULTs in mediating the sulfation of 2-butoxyethanol or sorbitan monolaurate was examined. Taken together, these results implied that SULT-mediated sulfation may function in the detoxification of these two oil dispersant compounds.

Xu et al. (2017) evaluated the genotoxicity of 6 unspecified chemical dispersants used for marine oil spills. They used luminescent bacteria test (LBT) based on Acinetobacter sp. RecA combined with fish exposure experiment based on marine medaka (Oryzias melastigma) to detect the genotoxicity of 6 chemical dispersants. In the LBT, the 500 mg/L and 1 000 mg/L of chemical dispersant HLD-501 exhibited genotoxicity of 0.039 mg/L and 0.032 mg/L of mitomycin C (MMC), respectively. In addition, the DNA damage ratio of O. melastigma by the 6 chemical dispersants in the comet assay was in the order of concentrate type RS-II > concentrate type RS-I > conventional type HLD-501 > conventional type Fuken-2 > conventional type RS-I > conventional type Weipu. However, HLD-501 resulted in the most serious DNA damage (level 3), being the most genotoxic among the 6 dispersants. The result of these two methods for genotoxicity detection fitted well with each other.

Results from Previous Literature Reviews

2002 This section was combined with the oil and dispersant toxicity section.

2008 The results of dispersant toxicity testing are similar to that found in previous years, namely that dispersants vary in their toxicity to various species, however, dispersant toxicity is typically less than the toxicity of dispersed oil, by whatever tests. There are no studies departing from the traditional lethal aquatic toxicity assay and none that focus on the longer-term effects of short term exposures. There certainly is need for more of these types of studies. There is also a need to leave the traditional lethal assays and use some of the newer tests for genotoxicity, endocrine disruption and others.

2014 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.

3.2.3 General Effects on Biota and Wildlife

Introduction

This section separates the many aquatic toxicity studies as described above from the general studies and from those studies which are not strictly aquatic or includes species not typically studied in aquatic toxicity studies. This review saw the inception of more studies of the effects of dispersants and oil and dispersants on wildlife.

Summary and Conclusions

Studies in this time period showed similar results to previous studies that corals are very sensitive to oil and particularly dispersants and dispersed oil. This is caused by the fact that the external membrane of the coral is permeable to oil components and dispersants. Studies in the past two decades have repeated these findings. This should be cause to re-examine the use of dispersants in any area where the dispersed oil or dispersant can be carried to corals.

Other effects noted include:

- Several studies of the aftermath of the Deepwater Horizon spill show that deep-sea corals were damaged up to 14 km away from the drill site. This damage was largely caused by suffocation from oil mats and flocculent layers of oil.
- Some fish larvae are affected by dispersed oil, however others, such as mackerel larvae are not as sensitive.

- Turtles may be susceptible to oil and dispersants, however, tests have yet to be developed to show this.
- Marsh impacts by oil and dispersed oil were severe during the DWH spill, however the impacts of the dispersant are unknown.
- Birds eyes are affect by oil and dispersants.
- Dolphins do show genetic response to dispersed oil, however as in turtles, more testing is required.
- Mangroves may also show responses to dispersed oil, however, further work is necessary.

Detailed Study Summaries

Beyer and Trannum (2016) review the biological effects of the Deepwater Horizon spill including a brief review of the use of dispersants. Factors such as oil-biodegradation, ocean currents and response measures (dispersants, burning) reduced coastal oiling. Still, > 2100 km of shoreline and many coastal habitats were affected. Research shows that oiling caused a wide range of biological effects, although worst-case impact scenarios did not materialize in most cases. Biomarkers in individual organisms were more informative about oiling stress than population and community indices. Salt marshes and seabird populations were hard hit, but were also quite resilient to oiling effects. Monitoring demonstrated little contamination of seafood. Certain impacts are still understudied, such as effects on seagrass communities. Concerns of long-term impacts remain for large fish species, deep-sea corals, sea turtles and cetaceans.

Buskey et al. (2016) review the extensive studies on the Deepwater Horizon spill to determine the potential acute and sublethal toxic effects of crude oil and dispersants on a range of planktonic, nektonic, and benthic marine organisms. Organisms such as phytoplankton, zooplankton, and fish were examined via controlled laboratory studies, while others, such as deep-sea benthic invertebrates, which are difficult to sample, maintain, and study in the laboratory, were assessed through field studies. Laboratory studies with marine fishes focused on the sublethal effects of oil and dispersants, and early life history stages were generally found to be more sensitive to these toxins than adults. Field studies in the vicinity of the DWH spill indicate a significant reduction in abundance and diversity of benthic meiofauna and macrofauna as well as visual damage to deep-sea corals. Overall, studies indicate that while the responses of various marine species to oil and dispersants are quite variable, a general picture is emerging that chemical dispersants may be more toxic to some marine organisms than previously thought, and that small oil droplets created by dispersant use and directly consumed by marine organisms are often more toxic than crude oil alone.

The committee struck by the U.S. National Research Council (2014) summarized various impacts of the Deepwater Horizon spill including that on marshes and shorelines and on dolphins, a prime affected marine mammal. It was noted that the effects on the marshes was particularly severe. The death of dolphins particularly after the spill was disturbing, but direct links to the spill could not be made.

Etnoyer et al. (2016) surveyed hard-bottom 'mesophotic' reefs along the '40-fathom' (73 m) shelf edge in the northern Gulf of Mexico for potential effects of the Deepwater Horizon (DWH) oil spill from the Macondo well in April 2010. Alabama Alps Reef, Roughtongue Reef, and Yellowtail Reef were near the well, situated 60–88 m below floating oil discharged during the DWH spill for several weeks and subject to dispersant applications. In contrast, Coral Trees Reef and Madison Swanson South Reef were far from the DWH spill site and below the slick for less than a week or not at all, respectively. The reefs were surveyed by ROV in 2010, 2011, and 2014 and compared to similar surveys conducted one and two decades earlier. Large gorgonian octocorals were present at all sites in moderate abundance including Swiftia exserta, Hypnogorgia pendula, Thesea spp., and Placogorgia spp. The gorgonians were assessed for health and condition in a before-after-control-impact (BACI) research design using still images captured from ROV video transects. Injury was modeled as a categorical response to proximity and time using logistic regression. The condition of gorgonians at sites near the Macondo well declined significantly post-spill. Before the spill, injury was observed for 4–9 % of large gorgonians. After the spill, injury was observed in 38–50 % of large gorgonians. Odds of injury for sites near Macondo were 10.8 times higher post-spill, but unchanged at far sites. The majority of marked injured colonies in 2011 declined further in condition by 2014. Marked healthy colonies generally remained healthy. Background stresses to corals, including fishing activity, fishing debris, and coral predation, were noted during surveys, but do not appear to account for the decline in condition at study sites near Macondo well.

Fiorello et al. (2016) group captured common murres and exposed them to Corexit EC9500a, crude oil, or a combination in artificial seawater. They performed ophthalmic examinations and measured intraocular pressures and tear production before and after exposure. They found that exposure to oil or dispersant was related to the development of conjunctivitis and corneal ulcers. Odds ratios for birds exposed to oil or dispersant were positive and significant for the development of conjunctivitis, while odds ratios for the development of corneal ulcers were positive and significant only for birds exposed to a high concentration of oil. Ocular exposure to dispersants and petroleum in seabirds may cause conjunctivitis and may play a role in the development of corneal ulcers.

Fisher et al. (2014, 2016) review Natural Resource Damage Assessment studies and follow-up work funded as part of the Gulf of Mexico Research Initiative that targeted deep water pelagic and benthic fauna. Oil was incorporated into the pelagic food web, and a reduction in planktonic grazers led to phytoplankton blooms. Fish larvae were killed, and a generation may have been lost. Cetaceans were killed, and many avoided the area of the spill. In the benthic realm, there was a large loss of diversity of soft-bottom infauna, which were still not recovering a year after the DWH oil spill. Colonial octocorals that are anchored to the hard seafloor and are especially vulnerable to anthropogenic impact, died as a result of being covered with flocculent material containing oil and dispersant. Soft- and hard-bottom effects of the oil spill were found as much as 14 km away from the DWH wellhead site. Deep-sea communities in the Gulf of Mexico are diverse, play critical roles in the food web and carbon cycling, affect productivity, are sensitive to perturbations, and are at risk to contaminant exposure

Girard et al. (2016) focused on the influence of the ophiuroid symbiont *Asteroschema clavigerum* (star fish associated with coral), on the resilience of its octocoral host *Paramuricea biscaya* after the Deepwater Horizon oil spill in the Gulf of Mexico. Corals were imaged between 2011 and 2014 at 4 sites, 3 of which were impacted by the spill. Each colony was digitized to quantify the impact on corals. They developed a method to define an area under the influence of ophiuroids for each coral colony. The level of total visible impact, as well as recovery, was then compared within and outside this area. For the majority of colonies, recovery from visible impact and hydroid colonization was negatively correlated with distance from the ophiuroid. Total visible impact was lower within the area influenced by ophiuroids, and branches within this area were more likely to recover. These results indicate that P. biscaya benefits from its association with A. clavigerum, likely through the physical action of ophiuroids removing material depositing on polyps, and perhaps inhibiting the settlement of hydroids.

Hernandez et al. (2016) studied the effects of the Deepwater Horizon spill on larval Red Snapper, data from a long-term ichthyoplankton survey off the coast of Alabama examining: (1) larval abundances among pre-impact (2007-2009), impact (2010), and post-impact (2011, 2013) periods; (2) proxies for larval condition (size-adjusted morphometric relationships and dry weight) among the same periods; and (3) the effects of background environmental variation on larval condition. They found that larval Red Snapper were in poorer body condition during 2010, 2011, and 2013 as compared to the 2007-2009 period, a trend that was strongly and negatively related to variation in Mobile Bay freshwater discharge. However, larvae collected during and after 2010 were in relatively poor condition even after accounting for variation in freshwater discharge and other environmental variables. By contrast, no differences in larval abundance were detected during these survey years. Taken together, larval supply did not change relative to the timing of the DWH, but larval condition was negatively impacted. Even small changes in condition can affect larval survival, so these trends may have consequences for recruitment of larvae to juvenile and adult life stages.

Ozhan et al. carried out a literature review of phytoplankton responses to the Macondo (Deepwater Horizon) oil spill indicate that the phytoplankton may have been stimulated by the oil spill, although the presence of low-salinity water in the region makes it difficult to discount the importance of riverine-borne nutrients as a factor. A few studies suggest that the oil spill was toxic to some phytoplankton species, whereas others indicate that the degree of tolerance to the oil or to dispersants differs among species. These results generally comply with findings of previous studies, but a lack of published field data analyses prevents further assessment of the impacts of the Deepwater Horizon oil spill on phytoplankton population dynamics in the northern Gulf of Mexico.

Prouty et al. (2016) continued their study of the impact of the April 2010 Deepwater Horizon spill on deep-sea coral communities in the Gulf of Mexico. Impacts from the spill include observation of corals covered with flocculent material, with bare skeleton, excessive mucous production, sloughing tissue, and subsequent colonization of damaged areas by hydrozoans. Information on growth rates and life spans of deep-sea corals is important for understanding the vulnerability of these ecosystems to both natural and anthropogenic perturbations, as well as the likely duration of any observed adverse impacts. They report radiocarbon ages and radial and linear growth rates based on octocorals (Paramuricea spp. and Chrysogorgia sp.) collected in 2010 and 2011 from areas of the DWH impact. The oldest coral radiocarbon ages were measured on specimens collected 11 km to the SW of the oil spill from the Mississippi Canyon spill site: 599 and 55 calendar years BP, suggesting continuous life spans of over 600 years for Paramuricea biscaya, the dominant coral species in the region. Calculated radial growth rates, between 0.34 $\mu m\ yr^{-1}$ and 14.20 $\mu m\ yr^{-1}$, are consistent with previously reported proteinaceous corals from the Gulf. Anomalously low radiocarbon ($\delta^{14}C$) values for soft tissue from some corals indicate that these corals were feeding on particulate organic carbon derived from an admixture of modern surface carbon and a low ^{14}C carbon source. Results from this work indicate fossil carbon could contribute 5-10% to the coral soft tissue $\delta^{14}C$ signal within the area of the spill impact. The influence of a low ^{14}C carbon source (e.g., petro-carbon) on the particulate organic carbon pool was observed at all sites within 30 km of the spill site, with the exception of MC118, which may have been outside of the dominant northeast-southwest zone of impact. The quantitatively assessed extreme longevity and slow growth rates documented here highlight the vulnerability of these long-lived deep-sea coral species to disturbance.

Rabalais and Turner (2016) synthesized key results of published research on the oiling effects on coastal habitats in the Gulf of Mexico as a result of the Deepwater Horizon spill. There were immediate negative impacts in the moderately to heavily oiled marshes, and on the resident fish and invertebrates. Recovery occurred in many areas within the two years following the oiling and continues, but permanent damage from heavily oiled marshes resulted in eroded shorelines. Organisms, including microbial communities, invertebrates, and vertebrates, were diminished by acute and chronic hydrocarbon exposure. However, the inherent variability in populations and levels of exposure, compounded with multiple stressors, often masked what were expected, predictable impacts. The effects are expected to continue to some degree with legacy hydrocarbons, or the marsh ecosystem will reach a new baseline condition in heavily damaged areas.

Ransom et al. (2016) reviewed Spanish Mackerel in context with the Deepwater Horizon oil spill that coincided with the pelagic larval stages of many valued commercial and recreational fishes in the northern Gulf of Mexico. Larval fish survival and eventual recruitment into adult populations may have been impacted directly through toxicity or indirectly through changes in the planktonic food web caused by the release of oil and chemical dispersants during the DWH event. Using samples from a long-term ichthyoplankton survey off the coast of Alabama, in a region impacted by the DWH spill, the abundance and condition of larval Spanish mackerel *Scomberomorus maculatus* were compared during summer months in years before (2007-2009), during (2010) and after (2011) the DWHOS. Changes in larval quality were examined using morphometric and weight-based body condition indices, whereas potential trophic impacts were quantified using stable C and N isotopes. Larval abundance did not differ across years. However, larvae were in better body condition during the DWH period relative to before the spill. Larvae had generally similar isotopic values through time. Thus, larval Spanish mackerel body condition was largely resilient to the harmful effects of the DWH spill.

Ross and Hallock (2014) developed bioassay protocols for chemical pollutants utilizing *Amphistegina gibbosa d'Orbigny*, the coral species found ubiquitously on Caribbean and western Atlantic reefs. A protocol was developed to identify the 48-h Lethal Concentration LC_{50}, the concentration of a test chemical in seawater that killed 50% of the specimens during 48-h exposure. Two chemicals found in oil dispersants employed in the clean-up efforts in the Gulf of Mexico, propylene glycol and 2-butoxyethanol, were used as test chemicals. Some individuals, which had appeared to be dead at the end of the 48-h exposure period, recovered following rinsing and removal to clean seawater. This observation required further definition of an Acute Concentration AC_{50}, the concentration of chemical in seawater that killed or rendered inactive

50% of the specimens during a 48-hour exposure. They also evaluated several indicators of chronic effects of the short-term exposure. All concentrations of propylene glycol tested resulted in significantly higher incidences of bleaching (color loss in the foraminifers due to loss of, or damage to, algal symbionts). As bleaching is a common stress response in zooxanthellate corals, even short-term exposure to dispersant chemicals may increase susceptibility to bleaching.

Sinski et al. (2016) assessed the contamination of the DWH spill occurred in offshore waters considered important for blue crab larval development where there was high spatial and temporal overlap between blue crab larvae and the incident area. Exposure to contaminants may have occurred in both the offshore developmental phase and the nearshore settlement stage. Fluorescence spectroscopy techniques were developed to detect polycyclic aromatic hydrocarbon contamination in composite samples of tissue of 50 megalopae. Samples as low as 400 μl were analyzed allowing for detection of contaminants in very small sample sizes. Evidence of petroleum contamination was found in all megalopae harvested from the wild.

Tansel et al. (2015) evaluated the effect of crude oil on water transport through mangroves roots in the presence and absence of dispersants. Water transport through the roots was evaluated experimentally using red mangrove root segments exposed to salt water contaminated with Louisiana crude oil for seven days in the presence and absence of Corexit 9500A. Experimental observations were interpreted in view of the structural integrity and fouling phenomena observed on the epidermis and endodermis layers of the roots. The effects of oil on the radial water flux through the epidermis and endodermis were analyzed using a dual layer filtration model. Progression of fouling due to accumulation and penetration of the contaminants through the root layers were interpreted in relation to observed mangrove health (long and short-term effects) reported in the literature.

Vander Zanden et al. (2016) used long-term biological tissue records to provide pre-disaster data for a vulnerable marine organism, the sea turtle. Keratin samples from the carapace of loggerhead sea turtles record the foraging history for up to 18 years, allowing them to evaluate the effect of the oil spill on sea turtle foraging patterns. Samples were collected from 76 satellite-tracked adult loggerheads in 2011 and 2012, approximately one to two years after the spill. Of the 10 individuals that foraged in areas exposed to surface oil, none demonstrated significant changes in foraging patterns post spill. The observed long-term fidelity to foraging sites indicates that loggerheads in the northern Gulf of Mexico likely remained in established foraging sites, regardless of the introduction of oil and chemical dispersants. More research is needed to address potential long-term health consequences to turtles in this region.

White et al. (2016) examined the immunotoxicity of Louisiana sweet crude oil and the chemical dispersant Corexit using lymphocyte proliferation (LP) and natural killer cell (NK) assays as measures of impact on the adaptive (LP) and innate (NK) immune response in bottlenose dolphins. Study results show that both high-energy media-accommodated fractions (MAF) and chemically enhanced MAF (CEMAF) mixtures modulate immune function. Following exposure to Louisiana sweet crude, both B- and T-cell proliferation of white blood cells was increased for all exposure concentrations, compared to control; however, this increase was only significant for the 50% and 100% treatments. In contrast, exposure of white blood cells to the CEMAF mixture significantly decreased both T- and B-cell proliferation in the 25%, 50% and 100% treatments. NK cell activity was enhanced significantly by CEMAF mixtures for the

50% and 100% treatments. The immunosuppression of LP at environmentally relevant concentrations of oil and dispersant suggests that marine mammals may be unable to mount an adequate defense against xenobiotic threats following exposure to oil and dispersant, leaving them more susceptible to disease. In contrast, NK cell activity was significantly enhanced, which may increase an organism's tumor or viral surveillance ability by mounting an enhanced immune response.

Yednock et al. (2015) sequenced transcriptomes from hepatopancreas and gill tissues of juvenile blue crabs after exposing them to a water-accommodated fraction of surrogate Macondo crude oil in the laboratory and compared them to transcriptomes from an unexposed control group. Illumina sequencing provided 42.5 million paired-end sequencing reads for the control group and 44.9 million paired-end reads for the treatment group. From these, 73,473 transcripts and 52,663 genes were assembled. Comparison of control and treatment transcriptomes revealed about 100 genes from each tissue type that were differentially expressed. However, a much larger number of transcripts, approximately 2000 from each tissue type, were differentially expressed. Several examples of alternatively spliced transcripts were verified by qPCR, some of which showed significantly different expression patterns. The combined transcriptome from all tissues and individuals was annotated to assign putative gene products to both major gene ontology categories as well as specific roles in responses to cold and heat, metabolism of xenobiotic compounds, defense, hypoxia, osmoregulation and ecdysis. Among the annotations for upregulated and alternatively-spliced genes were candidates for the metabolism of oil-derived compounds. It was found that previously, few genomic resources were available for blue crabs or related brachyuran crabs. The transcriptome sequences reported here represent a major new resource for research on the biology of blue crabs. These sequences can be used for studies of differential gene expression or as a source of genetic markers. Genes identified and annotated in this study include candidates for responses of the blue crab to xenobiotic compounds, which could serve as biomarkers for oil exposure. Changes in gene expression also suggest other physiological changes that may occur as the result of exposure to oil.

Ylitalo et al. (2017) collected substances from the skin of oiled and suspected oiled turtles and analyzed them for petroleum hydrocarbons to determine oiling status and oil sources. Tissue, gastroenteric and bile samples from a subset of visibly oiled and unoiled turtles that died during the spill in 2010 and in 2011 were analyzed for evidence of internal exposure and absorption of polycyclic aromatic hydrocarbons (PAHs) and the dispersant component dioctyl sodium sulfosuccinate (DOSS). The volume of external oil collected from sea turtles was sufficient to confirm the presence of petroleum on 61% of turtles, and oil from the DWH spill was identified as the source in 97% of those turtles in which conclusive comparison was possible. Visibly oiled turtles had higher concentrations of tissue PAH or biliary fluorescent PAH metabolites compared to those determined in unoiled animals. Findings in most of the unoiled turtles were suggestive of low-level PAH exposure from various sources that may represent background values for sea turtles from the northern GoM. DOSS levels were below the limit of quantitation in all samples analyzed except in an esophagus sample of a heavily oiled sea turtle. Overall, the results for petroleum or petroleum-derived compounds of both external and internal samples of sea turtles supported visual observations of oiling.

Results from Previous Literature Reviews
2002 Several studies were carried out and it was found that dispersants were toxic to corals, much more so than oil.

2008 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. Studies found that dispersed oil and the dispersants were significantly more toxic than crude oil by itself.

2014 Coral reefs are noted as being very sensitive to oil or especially dispersants because the tissue over the skeleton is very thin and dispersants appear to enhance the penetration of oil components.

3.2.4 Photo-enhanced Toxicity

Introduction

Several researchers have noted that oil and especially dispersed oil has greater toxicity when exposed to UV or UV components of natural sunlight (Fingas, 2014). This typically involves a transparent life phase which is on or near the water surface.

Summary and Conclusions

Certain biota have transparent life phases and spend portions of their life near or on the sea surface. Some biota are prone to photo-enhanced toxicity. Photo-enhanced toxicity consists of two mechanisms, but the most important one is photosensitization. This occurs when a PAH absorbs energy from the light and then transfers this to dissolved oxygen. This results in enhanced toxicity to many organisms. The tests of photo-enhanced toxicity show that oil and especially dispersed oil is increased by UV light. Increases of 1.5 to 4 for noted for physically-dispersed oil and from about 4 to 48 times for chemically-dispersed oil. This photo-enhanced toxicity is particularly applicable to dispersant application in shallow waters.

Detailed Study Summary

Almeda et al. (2016a) determined the influence of natural ultraviolet B (UVB) radiation on the lethal and sublethal toxicity of dispersed crude oil to naupliar stages of the planktonic copepods *Acartia tonsa*, *Temora turbinata* and *Pseudodiaptomus pelagicus*. Low concentrations of dispersed crude oil (1 μL/L) caused a significant reduction in survival, growth and swimming activity of copepod nauplii after 48 h of exposure. UVB radiation increased toxicity of dispersed crude oil by 1.3-3.8 times, depending on the experiment and measured variables. Ingestion of crude oil droplets may increase photoenhanced toxicity of crude oil to copepod nauplii by enhancing photosensitization. Photoenhanced sublethal toxicity was significantly higher when T. turbinata nauplii were exposed to dispersant-treated oil than crude oil alone, suggesting that chemical dispersion of crude oil may promote photoenhanced toxicity to marine zooplankton. The results demonstrate that acute exposure to concentrations of dispersed crude oil and dispersant (Corexit 9500) commonly found in the sea after oil spills are highly toxic to copepod nauplii and that natural levels of UVB radiation substantially increase the toxicity of crude oil to these planktonic organisms.

Results from Previous Literature Reviews
2002 No findings on this topic.

2008 Several laboratory studies indicate that PAH toxicity increases (from about 12 to about 50,000 times) in exposures conducted with UV light present as it would be in nature in shallow waters. Photo-enhanced toxicity consists of two mechanisms, but the most important one is photosensitization. This occurs when a PAH absorbs energy from the light and then transfers this to dissolved oxygen. This results in enhanced toxicity to many organisms. The few tests of photo-enhanced toxicity clearly show that oil and especially dispersed oil is increased by UV light. Increases of 1.5 to 4 for noted for physically-dispersed oil and from about 4 to 48 times for chemically-dispersed oil. This photo-enhanced toxicity is particularly applicable to dispersant application in shallow waters.

2014 Several researchers have noted that oil and especially dispersed oil has greater toxicity when exposed to UV or UV components of natural sunlight. In the time period of this literature study there were no specific tests on this facet of toxicity.

3.2.5 Testing Protocols

Introduction

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

Summary and Conclusions

CROSERF aquatic testing protocols have been around for more than two decades and were developed in an era of lesser analytical capability. They have never been fully characterized in terms of modern analytical standards. It is suggested that the protocols be re-evaluated with the current analytical and droplet size measurement capabilities.

Detailed Study Summaries

Bejarano et al. (2015) carried out a quantitative review to evaluate the use of standard toxicity testing data to help inform decisions regarding dispersant use, recognizing some key issues with current practices, specifically, reporting toxicity metrics (nominal vs measured), exposure duration (standard durations vs short-term exposures), and exposure concentrations (constant vs spiked). Analytical chemistry data were used to demonstrate the role of oil loading on acute toxicity and the influence of dispersants on chemical partitioning. The analyses presented here suggest that decisions should be made on the basis of measured aqueous exposure concentrations and preferably, using data from short-term exposure durations under spiked exposure concentrations.

Forth et al. (2016) report on the creation of 4 Deepwater Horizon oils, which encompassed a range of weathering states, and 3 different oil-in-water mixing methods, for a total of 12 unique water accommodated fractions (WAFs). The study reported on the chemical characteristics of these 4 Deepwater Horizon oils and 12 WAFs. In addition, to better understand exposure chemistry, an examination was conducted of the effects of WAF preparation parameters-including mixing energy, starting oil composition, and oil-to-water mixing ratios-on the chemical profiles and final concentrations of these 12 WAFs. The results showed that the more weathered the starting oil, the lower the concentrations of the oil constituents in the WAF, with a shift in composition to the less soluble compounds. In addition, higher mixing energies increased the presence of insoluble oil constituents. Finally, at low to mid oil-to-water mixing ratios, the concentration and composition of the WAFs changed with changing mixing ratios; this change was not observed at higher mixing ratios (i.e., >1g oil/L).

Examination of the CROSERF protocols by Sandoval et al. (2017) showed some concern. The key aim of the Sandoval et al. study was compare and contrast the physical and chemical compositions of oil water mixtures prepared using fresh and weathered Macondo-related oils under different conditions of mixing and in the presence/absence of chemical dispersants. All samples were assessed for the presence of droplets, droplet size distribution, and detailed chemical composition including polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbon by fluorescence (TPHF). Preparations were also tested for stability over a 96-h period relevant to acute toxicity tests. The results indicate that water accommodated fractions (WAFs) produced consistent, droplet free solutions with concentration that represented the soluble components of the oil used. As expected, chemically-enhanced WAFs (CEWAFs) and high-energy WAFs (HEWAFs) generated large amounts of micron-size droplets and their chemical composition corresponded closely with that of the whole oil. However, the HEWAFs were highly dynamic, and unlike CEWAFs, much of the oil resurfaced within few hours of the initial preparation. Viscosity and lack of dispersability are the limiting factors for preparation of CEWAFs with weathered oils, in contrast HEWAFs did effectively introduce large amounts of weathered oil droplets in the test media. Despite this benefit, droplet sizes significantly decreased in HEWAFs with increase in weathering of the oil creating an additional variable to consider. Because the contribution of small droplets to toxicity is a topic that needs further investigation, the interpretation of results from high-energy preparations needs to be further evaluated. When the TPAHs concentrations of all preparations at all loadings were compared with the publicly available water-column data for samples analyzed during and after the DWH incident response they all ranked above the vast majority of the 10,828 samples reported during the actual spill. This leads to the conclusion that current methods of oil-water preparations are variable and may not be representative of actual conditions.

Results from Previous Literature Reviews

2002 This section was not included.

2008 CROSERF is noted. There have been a number of discussions on toxicity testing protocols. One note is that the protocols in the oil spill field have not kept pace with the researchers in the field. Another note is that there are many protocols in the literature, and the field of oil spill research appears to still use old protocols largely focused on acute lethal assays.

2014 The CROSERF protocols are noted as above.

3.3 Biodegradation

Introduction

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 affects the observed biodegradation rate. Many of the older studies that observed stimulation may have been confounded by the growth on the dispersants themselves as some of the surfactants are readily biodegradable. The effect of the dispersants on the oil biodegradation rate is most sensitive to the characteristics of the dispersant itself, even if all other factors are kept constant. 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 (Fingas, 2014).

Summary and Conclusions

Overall, one might note that many of the experimental systems used to investigate biodegradation might be inappropriate to represent the environment, because they apply high mixing energy in an enclosed, nutrient-sufficient environment and do not allow 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 (Fingas, 2014). 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, 2014 and references therein). 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 cannot analyze for many 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.

This present review found that most authors conclude that most studies found that dispersants suppress biodegradation. Table 3 shows summary of controlled studies. This present review rated 11% of the reviewed papers as showing neutral results; 22 % as showing positive results (notably all industry funded) and 67% of the rated studies as showing suppression of biodegradation by the presence of dispersants. These results are shown in Figure 2. These results are consistent with past reviews.

In addition, the following points are noted:

- When components of dispersants were tested separately, often these components had differing effects on the inhibition or promotion of biodegradation.
- Toxicity to some species of microbial biodegraders may be a factor that causes these varying results.
- There is a species shift with dispersants involved, as will be shown in the next section.
- Deep sea biodegradation may involve different dynamics than surface biodegradation and may require separate tools to investigate these matters further.

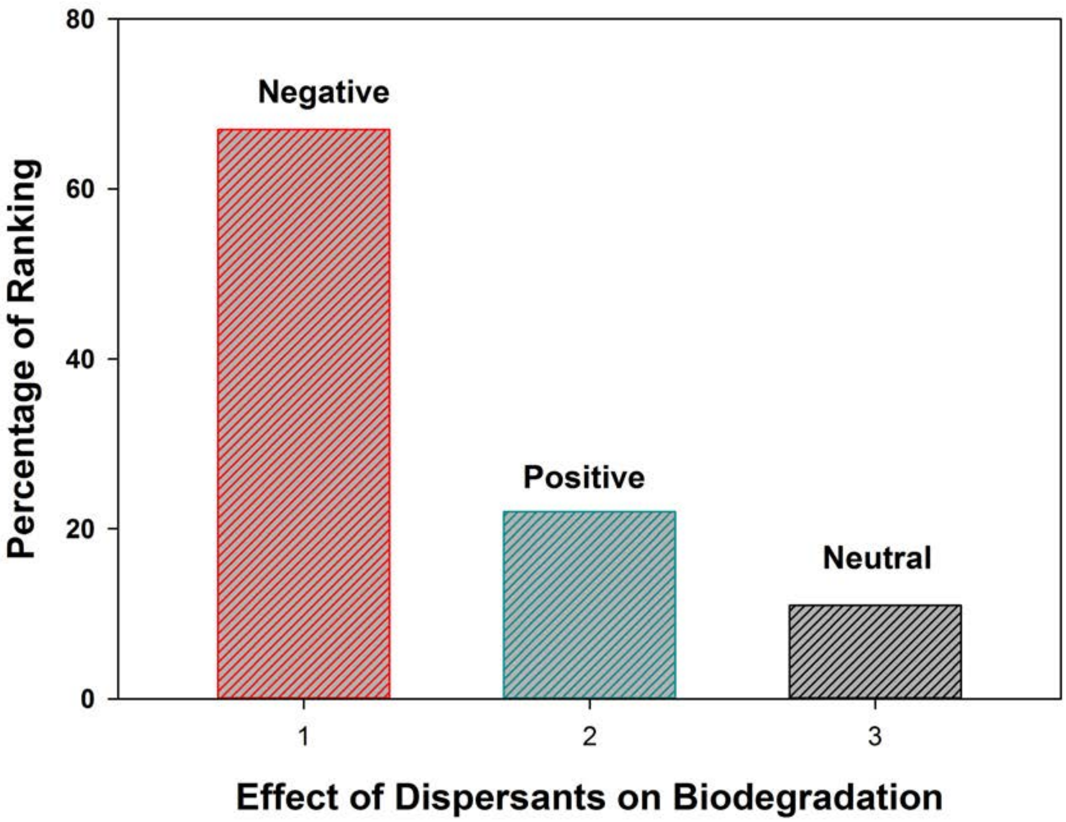

Figure 2 The ratings of the detailed studies as to the effect that chemical dispersion had on biodegradation. Sixty-seven percent of studies showed inhibition of degradation, 22% as promoting biodegradation and 11% as having mixed or neutral effects.

Detailed Study Summaries

Bagby et al. (2017) assessed the compound-specific rates of biodegradation for 125 aliphatic, aromatic, and biomarker petroleum hydrocarbons that settled to the deep ocean floor following release from the Macondo well blowout. Based on study of up to 168 distinct hydrocarbon analytes in 2,980 sediment samples collected within 4 years of the spill, a Macondo oil "fingerprint", they developed and identified a subset of 312 surficial samples consistent with contamination by Macondo oil. Three trends emerged from analysis of the biodegradation rates of 125 individual hydrocarbons in these samples. First, molecular structure served to effect biodegradation in a predictable fashion, with the simplest structures subject to fastest loss, indicating that biodegradation in the deep ocean progresses similarly to other environments. Second, for many alkanes and polycyclic aromatic hydrocarbons biodegradation occurred in two distinct phases, consistent with rapid loss while oil particles remained suspended, followed by slow loss after deposition to the seafloor. Third, the extent of biodegradation for any given sample was influenced by the hydrocarbon content, leading to substantially greater hydrocarbon persistence among the more highly contaminated samples. In other words, the more hydrocarbons, the less the biodegradation. In addition, under some conditions they found strong evidence for extensive degradation of numerous petroleum biomarkers, notably including the native internal standard 17α(H),21β(H)-hopane, commonly used to calculate the extent of oil weathering. This implies that work where only this hopane was used to perform studies may be in error.

Bagby et al. (2016) also speculated on the possible effect of dispersants on biodegradation. While it might appear that keeping the droplets suspended for longer in the water column would increase biodegradation, there is no evidence in this case that that was actually a fact in this case. Further, it was noted that there are studies showing some contrary evidence.

Hazen et al. (2016) reviewed marine oil biodegradation with emphasis on the positive benefits of dispersants. They note that catastrophic oil spills stimulate these biodegradation organisms to bloom in a reproducible fashion, and although oil does not provide bioavailable nitrogen, phosphorus or iron, there are enough of these nutrients in the sea that when dispersed oil droplets dilute to low concentrations these low levels are adequate for microbial growth. Most of the hydrocarbons in dispersed oil are degraded in aerobic marine waters with a half-life of days to months. In contrast, oil that reaches shorelines is likely to be too concentrated, have lower levels of nutrients, and have a far longer residence time in the environment. Oil that becomes entrained in anaerobic sediments is also likely to have a long residence time, although it too will eventually be biodegraded.

Bacosa et al. (2015a) determined the contributions of photooxidation and biodegradation to the weathering of Light Louisiana Sweet crude oil by incubating surface water from the Deepwater Horizon site under natural sunlight and temperature conditions. N-alkane biodegradation rate constants were about ten-fold higher than the photooxidation rate constants. For the 2-3 ring and 4-5 ring polycyclic aromatic hydrocarbons (PAHs), photooxidation rate constants were 0.08-0.98/day and 0.01-0.07/day, respectively. The dispersant Corexit enhanced degradation of n-alkanes but not of PAHs. Compared to biodegradation, photooxidation increased transformation of 4-5 ring PAHs by 70% and 3-4 ring alkylated PAHs by 36%. Sunlight inhibited biodegradation of pristane and phytane, possibly due to inhibition of the bacteria that can degrade branched-alkanes.

Bacosa et al. (2015b) incubated surface water from the DWH site with addition of crude oil, Corexit dispersant, or both for 36 days under natural sunlight in the northern Gulf of Mexico. The bacterial community was analyzed over time for total abundance, density of alkane and polycyclic aromatic hydrocarbon degraders, and community composition via pyrosequencing. The results showed that, for treatments with oil and/or Corexit, sunlight significantly reduced bacterial diversity and evenness and was a key driver of shifts in bacterial community structure. In samples containing oil or dispersant, sunlight greatly reduced abundance of the Cyanobacterium Synechococcus but increased the relative abundances of Alteromonas, Marinobacter, Labrenzia, Sandarakinotalea, Bartonella, and Halomonas. Dark samples with oil were represented by members of Thalassobius, Winogradskyella, Alcanivorax, Formosa, Pseudomonas, Eubacterium, Erythrobacter, Natronocella, and Coxiella. Both oil and Corexit inhibited the Candidatus Pelagibacter with or without sunlight exposure. For the first time, they demonstrated the effects of light in structuring microbial communities in water with oil and/or Corexit.

Bookstaver et al. (2015) studied *Alcanivorax borkumensis*, a hydrocarbon degrading bacterium linked to oil degradation and its reaction to Corexit 9500. They built an experimental model to quantitatively measure the transient growth of Alcanivorax borkumensis at the interface of oil and water. This is the first study of how A. borkumensis interacts with a surfactant decorated oil-water interface. They used Corexit EC9500A, cetylytrimethylamonium bromide, dioctyl sulfosuccinate sodium salt, l-α-phosphatidylcholine, sodium dodecyl sulfate, and Tween 20 to investigate the impact of dispersants on *Alcanivorax borkumensis*. They assessed the impact of these dispersants on the growth rate, lag time, and maximum concentration of *Alcanivorax borkumensis*. They show that the charge, structure, and surface activity of these surfactants greatly impact the growth of A. borkumensis. Their results indicated that out of the surfactants tested only Tween 20 assists Acanivorax borkumensis growth, the remaining ingredients slowed the growth of the bacterium.

Oil spill microcosms experiments were carried out by Capello et al. (2014) to evaluate the effect of bioemulsificant exopolysaccharide (EPS2003) on quick stimulation of hydrocarbonoclastic bacteria. The early hours of oil spill, were stimulated using an experimental seawater microcosm, supplemented with crude oil and EPS2003; this system was monitored for 2 days and compared to control microcosm (only oil-polluted seawater). Determination of bacterial abundance, heterotrophic cultivable and hydrocarbon-degrading bacteria were carried out. Community composition of marine bacterioplankton was determined by 16S rRNA gene clone libraries. Data obtained indicated that bioemulsificant addition stimulated an increase of total bacterial abundance and, in particular, selection of bacteria related to Alcanivorax genus; confirming that EPS2003 could be used for the dispersion of oil slicks and could stimulate the selection of marine hydrocarbon degraders thus increasing bioremediation process.

Kleindienst et al. (2016c) simulated environmental conditions comparable to the hydrocarbon-rich, 1,100 m deep plume that formed during the Deepwater Horizon discharge. The presence of dispersant significantly altered the microbial community composition through selection for potential dispersant-degrading Colwellia, which also bloomed in situ in Gulf deep waters during the discharge. In contrast, oil addition to Deepwater samples in the absence of dispersant stimulated growth of natural hydrocarbon-degrading Marinobacter. In these Deepwater microcosm experiments, dispersants did not enhance heterotrophic microbial activity or hydrocarbon oxidation rates. An experiment with surface seawater from an anthropogenically derived oil slick corroborated the Deepwater microcosm results as inhibition of hydrocarbon turnover was observed in the presence of dispersants, suggesting that the microcosm findings are broadly applicable across marine habitats. Extrapolating this comprehensive dataset to real world scenarios questions whether dispersants stimulate microbial oil degradation in deep ocean waters and instead highlights that dispersants can exert a negative effect on microbial hydrocarbon degradation rates.

Olson et al. (2017) used replicate laboratory microcosms to conduct weathering experiments to study the weathering of oil and the effects of dispersants on oil weathering. Fresh MC252 oil was evaporatively weathered 40% by-weight to approximate the composition of oil seen in surface slicks during the 2010 spill. This surface oil was then well mixed with two types of seawater, autoclaved artificial seawater, the abiotic control, and Gulf of Mexico seawater, the biotic experiment. Four different weathering combinations were tested: 10 mg of oil mixed in 150 ml artificial seawater (OAS) or natural (i.e., GoM) seawater (ON) and 10 mg of oil with dispersant mixed with 150 ml of artificial seawater (OASD) or natural seawater (OND). For the treatments with dispersant (OASD and OND), the dispersant-to-oil ratio was 1:20. The experiment was carried out over 28 days with replicates that were sacrificed on Days 0, 0.5, 3, 7, 14, 21 and 28. For the OAS and OASD treatments, abiotic weathering (i.e., evaporation) dominated the weathering process. However, the ON and OND treatments showed a dramatic and rapid decrease in total concentrations of both alkanes and aromatics with biodegradation dominating the weathering process. Further, there were no identifiable differences in the observed weathering patterns between microcosms using oil or oil treated with dispersant. In the biotic weathering microcosms, the relative degree of individual polycyclic aromatic hydrocarbon (PAH) depletion decreases with an increase in rings and within a homolog series (increased alkylation). The n-C17/pristane and n-C18/phytane ratios rapidly decreased compared to the abiotic weathering experiments. The C2-dibenzothiophenes (DBT)/C2-phenanthrenes (D2/P2) and C3-DBTs/C3-phenanthrenes (D3/P3) ratios initially remained constant during the early stages of weathering and then increased with time showing preferential weathering of the sulfur containing compounds compared to similar sized PAH compounds. These ratios in the abiotic microcosms remained constant over 28 days. Additionally, twenty-four quantitative MC252 oil biomarker ratios were evaluated to determine if their usefulness as oil source-fingerprinting tools were compromised after significant weathering and dispersant augmentation.

Ortmann and Lu ((2015) characterized the short-term response of coastal bacteria to dispersant, oil and dispersed oil was characterized using 16S rRNA gene tags in two mesocosm experiments conducted two months apart. Despite differences in the amounts of oil-derived alkanes across the treatments and experiments, increases in the contributions of hydrocarbon degrading taxa and decreases in common estuarine bacteria were observed in response to dispersant and/or oil. Between the two experiments, the direction and rates of changes in particulate alkane concentrations differed, as did the magnitude of the bacterial response to oil and/or dispersant. Together, the data underscore large variability in bacterial responses to hydrocarbon pollutants, implying that bioremediation success varies with starting biological and environmental conditions

Overholt et al. (2016) utilized two environmentally relevant species of hydrocarbon-degrading bacteria to quantify the response to Macondo crude oil and Corexit 9500A-dispersed oil in terms of bacterial growth and oil degradation potential. In addition, specific hydrocarbon compounds were quantified in the dissolved phase of the medium and linked to ecotoxicity using a U.S. Environmental Protection Agency-approved rotifer assay. Bacterial treatment significantly and drastically reduced the toxicity associated with dispersed oil (increasing the 50% lethal concentration [LC_{50}] by 215%). The growth and crude oil degradation potential of Acinetobacter were inhibited by Corexit by 34% and 40%, respectively; conversely, Corexit significantly enhanced the growth of Alcanivorax by 10% relative to that in undispersed oil. Furthermore, both bacterial strains were shown to grow with Corexit as the sole carbon and energy source. Hydrocarbon-degrading bacterial species demonstrate a unique response to dispersed oil compared to their response to crude oil, with potentially opposing effects on toxicity. While some species have the potential to enhance the toxicity of crude oil by producing biosurfactants, the same bacteria may reduce the toxicity associated with dispersed oil through degradation or sequestration.

Pendergraft and Rosenheim (2014) employed a ramped pyrolysis carbon isotope technique to investigate thermochemical and isotopic changes in organic material from coastal environments contaminated with oil from the 2010 BP Deepwater Horizon oil spill. Oiled beach sediment, tar ball, and marsh samples were collected from a barrier island and a brackish marsh in southeast Louisiana over a period of 881 days. Stable carbon (^{13}C) and radiocarbon (^{14}C) isotopic data demonstrate a predominance of oil-derived carbon in the organic material. Ramped pyrolysis profiles indicate that the organic material was transformed into more stable forms. The data indicate relative rates of stabilization in the following order, from fastest to slowest: high energy beach sediments > low energy beach sediments > marsh > tar balls. Oil was transformed most rapidly where shoreline energy and the rates of oil dispersion and exchange with water, sediments, microbes, oxygen, and nutrients were greatest. Still, isotope data reveal persistence of oil.

Pietroski et al. (2015) collected marsh soil samples in Louisiana after the DWH spill from an unimpacted marsh site proximal to coastal areas that suffered light to heavy oiling for a laboratory evaluation to determine the effect of Corexit on the wetland soil microbial biomass as well as N-mineralization and denitrification rates. Microbial biomass nitrogen (N) values were below detection for the 1:10, 1:100 and 1:1000 Corexit:wet soil treatments. The potentially mineralizable N (PMN) rate correlated with microbial biomass with significantly lower rates for the 1:10 and 1:100 Corexit:wet soil additions. Potential denitrification rates for Corexit:wet soil ratios after immediate dispersant exposure were below detection for the 1:10 treatment, while the 1:100 was 7.6 % of the control and the 1:1000 was 33 % of the control. The 1:100 treatment was not significantly different from the control. Denitrification rates measured after two weeks exposure to the surfactant found the 1:10 treatment still below detection limit and the 1:100 ratio was 12 % of the control. Results from this lab study suggest that chemical dispersants have the potential to negatively affect the wetland soil microbial biomass and resultant microbial activity. Consequences of exposure led to reductions in several important microbial-regulated ecosystem services including water quality improvement (denitrification) and ecosystem primary productivity (N-mineralization).

Prince et al. (2015) apparently show that three dispersants widely available in international stockpiles effectively stimulate biodegradation when compared to oil in floating slicks.

Rahsepar et al. (2016) study the effect of Corexit on oil biodegradation by alkane and/or aromatic degrading bacterial culture in artificial seawater at different dispersant to oil ratios (DORs). The results show that dispersant addition did not enhance oil biodegradation. At DOR 1:20, biodegradation was inhibited, especially when only the alkane degrading culture was present. With a combination of cultures, this inhibition was overcome after 10 days. This indicates that initial inhibition of oil biodegradation can be overcome when different bacteria are present in the environment. They conclude that the observed inhibition is related to the enhanced dissolution of aromatic compounds into the water, inhibiting the alkane degrading bacteria.

Table 3 Biodegradation Studies

Author(s)	Year	Type	Basis	Effect of Dispersant Addition: Alkanes	PAHs	Oil Type	Details	Water Sourc	Time	Conc. Oil	Dispersant	Conc. Disp.	Spec-iation	Notes	Funder	Effect
Bacosa et al.	2015a	Lab		some increase	no effect	Louisiana	More degradation in light	Field	36 d	200 mg/L	Corexit 9500	1:20	no		Gov't & Res.	neut.
Bacosa et al.	2015b	Lab		not done	not done	Louisiana	Light enhances or decrease bacterial growth	Field	36 d	200 mg/L	Corexit 9500	1:20	yes	Corexit inhibited some bacteria	Gov't & Res.	neg
Bagby et al.	2015	Field	Chem. Analy.	not done	not done	Macondo	Studied Macondo oil at bottom	Field		field	none	field	no		Gov't	
Bookstaver et al	2015	Lab	Speciation	not relevant	not relevant	Octane	Alcanivorax borkumensis growth suppressed	Lab	72 h		Corexit 9500		yes	Corexit inhibited the bacteria	Gov't & Res.	neg.
Brakstad et al.	2015	Lab	Chem. Analy.	increase <size	no effect	Macondo	Changed droplet size 10 or 30 µm	Field	64 d	ns	Corexit 9500	ns	no	smaller droplets degraded more	Industry	pos.
Cappello et al.	2014	Lab	Speciation	not relevant	not relevant	Arabian	Effect on microorganisms with biosurfactant	Field	2 d	ns	Biosurfacan	not relevant	yes	Biosurfactant increased microbes	Gov't & Res.	
Crisafi et al.	2016	Meso	Speciation +an		tph only	Arabian	Effect on microorganisms with washing	Field	14 d	ns	not specifie	ns	yes	Washing agent decreased microbes	Gov't & Res.	neg.
Cuny et al.	2015	Meso	Speciation +an		tph only	Russian	Effect on microorganisms and Biodeg.	Field	286 d	24 mg/L soil	Finasol	1:20	yes	Dispersant did not increase biodegradation	Gov't & Res.	neg.
Kleindienst et al	2016c	Lab	Speciation	measured	measured	Macondo	Effect on Degradation and Microbes	Field	6 wk	66 mg/L	Corexit 9500		yes	over 31 wks, dispersant suppressed biodegradation	Gov't & Res.	neg.
Olson et al.	2017	Lab	Chem. Analy.	measured	measured	Macondo	Effect of natural water and dispersants	Field & Lab	28 d	66 mg/L	Corexit 9500	1:20	no	natural seawater degraded, little diff with disp.	Gov't & Res.	neut.
Ortmann and Lu	2015	Meso	Speciation +an	measured	measured	Macondo	Effects of oil, dispersant and none	Field	5 d	0.5 ml/L	Corexit 9500	1:20	yes	Dispersant and oil changed microbial composition	Gov't & Res.	neg.
Overhold et al.	2016	Lab	Speciation +an	measured	only as TPH	Marlin	Effects of oil, dispersant on Alcanivorax	Lab	14 d	5 to 25 g/L	Corexit 9500	1:50	yes	Growth and biodegradation inhibited t by 34% and 40%	Gov't & Res.	neg.
Overhold et al.	2016	Lab	Speciation +an	measured	only as TPH	Marlin	Effects of oil, dispersant on Acinetobac	Lab	14 d	5 to 25 g/L	Corexit 9500	1:50	yes	Growth increased by 10%	Gov't & Res.	neg.
Pietroski et al.	2015	Lab	Mineralization	measurement of mineralization		Macondo	Samples of DWH oil marsh soil	Field	5 d	as field	Corexit 9500	variable	total	initial reduced mineralization by 12%	Gov't & Res.	neg.
Pietroski et al.	2015	Lab	Mineralization	measurement of mineralization		Macondo	Samples of DWH oil marsh soil	Field	5 d	as field	Corexit 9500	variable	total	after 2 weeks reduced mineralization by 88%	Gov't & Res.	neg.
Prince et al.	2015	Lab	Analysis	not specifically- respirometry		Alaskan NS	Ran bottle tests and approx. quantified	Field	62 d	2.5 µL/L	Corexit 9500	1:20	no	increased biodegradation over slick	Industry	pos.
Prince et al.	2015	Lab	Analysis	not specifically- respirometry		Alaskan NS	Ran bottle tests and approx. quantified	Field	62 d	2.5 µL/L	Finasol	1:20	no	increased biodegradation over slick	Industry	pos.
Prince et al.	2015	Lab	Analysis	not specifically- respirometry		Alaskan NS	Ran bottle tests and approx. quantified	Field	62 d	2.5 µL/L	Slickgone	1:20	no	increased biodegradation over slick	Industry	pos.
Rahsepar et al.	2016	Lab	Speciation +an	yes	yes	Macondo	Tested aromatic degrader	Lab + inn.	30-50 d	100 mg/L	Corexit 9500	1:20	yes	decreased biodegradation/ increased aromatics	Gov't & Res.	neg.
Rahsepar et al.	2016	Lab	Speciation +an	yes	yes	Macondo	Tested alkane degrader	Lab + inn.	30-50 d	100 mg/L	Corexit 9500	1:20	yes	decreased biodegradation/ increased aromatics	Gov't & Res.	neg.
Seidel et al.	2016	Lab	ESI–FT–ICR–MS		ESI–FT–ICR–MS	Marlin	Biodegradation by products	Deep S	6 wk	180 ml/L	Corexit 9500	1:10	no	Decreased biodegradation/ Little DOSS deg	Gov't & Res.	neg.
Størdal et al.	2015a	Lab	Speciation & numbers			Troll	Copepod with and without oiled feces	Field	48 h	2 µl/L	Natural disp	nr	yes	feces slowed biodegradation	Gov't & Res.	
Størdal et al.	2015a	Lab	Speciation & numbers		alkane analy.	Troll	Copepod with and without oiled feces	Field	48 h	2 µl/L	Natural disp	nr	yes	oiled feces increased biodegradation	Gov't & Res.	
Størdal et al.	2015b	Lab	Speciation & numbers			Troll	Copepod with and without oiled feces	Field	48 h	2 µl/L	Natural disp	nr	yes	feces slowed biodegradation	Gov't & Res.	
Størdal et al.	2015b	Lab	Speciation & numbers		alkane analy.	Troll	Copepod with and without oiled feces	Field	48 h	2 µl/L	Natural disp	nr	yes	oiled feces increased biodegradation	Gov't & Res.	

Scoma et al. (2016a) note that many questions about the fate of petroleum-hydrocarbons within deep-sea environments remain unanswered, as well as the main constraints limiting bioremediation under increased hydrostatic pressures and low temperatures. The microbial pathways fueling oil bioassimilation are unclear, and the mild upregulation observed for beta-oxidation-related genes in both water and sediments contrasts with the high amounts of alkanes present in the spilled oil. The fate of solid alkanes, hydrocarbon degradation rates and the reason why the most predominant hydrocarbonoclastic genera were not enriched at deep-sea despite being present at hydrocarbon seeps at the Gulf of Mexico have been largely overlooked. This - review points out the missing information in the field, proposing a holistic approach where in situ and ex situ studies are integrated to reveal the principal mechanisms accounting for deep-sea oil bioremediation.

Scoma et al. (2016b) describe and study *Alcanivorax borkumensis* a ubiquitous model organism for hydrocarbonoclastic bacteria, which dominates polluted surface waters. Its negligible presence in oil-contaminated deep waters (as observed during the Deepwater Horizon accident) raises the hypothesis that it may lack adaptive mechanisms to hydrostatic pressure. The type strain SK2 was tested under 0.1, 5 and 10 MPa (corresponding to surface water, 500 and 1000 m depth, respectively). While 5 MPa essentially inactivated SK2, further increase to 10 MPa triggered some resistance mechanism, as indicated by higher total and intact cell numbers. Under 10 MPa, SK2 upregulated the synthetic pathway of the osmolyte ectoine, whose concentration increased from 0.45 to 4.71 fmoles cell^{-1}. Central biosynthetic pathways such as cell replication, glyoxylate and Krebs cycles, amino acids metabolism and fatty acids biosynthesis, but not β-oxidation, were upregulated or unaffected at 10 MPa, although total cell number was remarkably lower with respect to 0.1 MPa. Concomitantly, expression of more than 50% of SK2 genes was downregulated, including genes related to ATP generation, respiration and protein translation. Thus, A. borkumensis lacks proper adaptation to higher pressures but activates resistance mechanisms. These consist in poorly efficient biosynthetic rather than energy-yielding degradation-related pathways, and suggest that HP does represent a major driver for its distribution at deep-sea.

Seidel et al. (2016) explore the biodegradation of oil, dispersant, dispersed oil or dispersed oil and nutrients at the molecular level using ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry following a laboratory experiment with Gulf deep water. Oil-derived molecular formulae exhibited a specific molecular fingerprint and were mainly observed in the mass range <300 Da. The relative abundance of heteroatom-containing (N, S, and P) compounds decreased over time in the oil-only treatments, indicating that they may have served as nutrients when oil-derived hydrocarbons were metabolized. Relative changes over time in the molecular composition were less pronounced in the dispersed oil treatments compared to the oil-only treatments, suggesting that dispersants affected the metabolic pathways of organic matter biodegradation. In particular, dispersant addition led to an increase of S-containing organic molecular formulae, likely derived from the surfactant di-octyl sulfosuccinate (DOSS). DOSS and several dispersant-derived metabolites (with and without S) were still detectable after six weeks of incubation, underscoring that they were not rapidly biodegraded under the experimental conditions. FT-ICR-MS fragmentation studies allowed tentatively assigning structures to several of these molecules, and the authors propose that they are degradation products of DOSS and other dispersant components. The present study suggests preferential degradation, transformation and enrichment of distinct dispersant molecules, highlighting the need to include these compounds when tracking Corexit-derived compounds in the environment.

Størdal et al. (2015) studied biotransformation of components in crude oil dispersions in the presence of feces from marine copepods. Dispersed oil was incubated alone, with the addition of clean or oil-containing feces. They hypothesized that the feces would contribute nutrients to bacteria, and result in higher concentrations of oil-degrading bacteria. Presence of clean feces resulted in higher degradation of aromatic oil compounds, but lower degradation of n-alkanes. Presence of oil-containing feces resulted in higher degradation of n-alkanes. The effect of clean feces on aromatic compounds are suggested to be due to higher concentrations of nutrients in the seawater where aromatic degradation takes place, while the lower degradation of n-alkanes is suggested to be due to a preference by bacteria for feces over these compounds. Large aggregates were observed in oil dispersions with clean feces, which may cause sedimentation of un-weathered lipophilic oil compounds towards the seafloor if formed during oil spills.

Størdal et al. (2015b) characterized feeding activity and microbial communities in feces from *Calanus finmarchicus* feeding in oil dispersions. Feeding activity was significantly reduced in oil dispersions. The microbial communities in clean and oil-containing copepod feces were dominated by Rhodobacteraceae family bacteria (Lesingera, Phaeobacter, Rugeria, and Sulfitobacter), which were suggested to be indigenous to copepod feces. The results also indicated that these bacteria were metabolizing oil compounds, as a significant increase in the concentrations of viable oil degrading microorganisms was observed in oil-containing feces. This study shows that bacteria in feces from copepods feeding in dilute oil dispersions have capacity for degradation of oil. Zooplankton may therefore contribute to weathering of oil by excreting feces with microbial communities already adapted to degradation of oil.

Results from Previous Literature Reviews

2002 One study was noted as finding that overall Corexit 9527 suppressed oil degradation (oxidation) while some of its components enhanced degradation and others suppressed degradation.

2008 The study noted that the effect of dispersants on biodegradation is a very important topic as one of the stated objectives of using dispersants is to increase biodegradation. The effects of surfactants and oil dispersants on the rate and extent of biodegradation of crude oil and individual hydrocarbons have been extensively investigated with mixed results. In some studies biodegradation is shown to be stimulated, in many there is inhibition and others observed no effects with the addition of dispersants or surfactants. The effect of surfactants and dispersants depends on the chemical characteristics of the dispersants, the hydrocarbons and the microbial community. Other factors such as nutrient concentrations, oil-water ratios and mixing energy also affects the observed biodegradation rate. Many of the older studies that observed stimulation may have been confounded by the growth on the dispersants themselves as some of the surfactants are readily biodegradable. The effect of the dispersants on the oil biodegradation rate is most sensitive to the characteristics of the dispersant itself, even if all other factors are kept constant. In one study, several specific surfactants were shown to inhibit the biodegradation of some classes of hydrocarbons. Only a few surfactants stimulated biodegradation in a culture taken from refinery sludge. NAS noted that other studies have shown complex interactions of oil, surfactant and conditions. One study showed that the ionic surfactant in Corexit 9527 and 9500 inhibited cultures of alkane-degrading bacteria. The non-ionic surfactants in the same mixture stimulated biodegradation. The variable effects of dispersants and surfactants on oil biodegradation are probably due to their effect on microbial uptake of hydrocarbons. It is clear that surfactants can interfere with the attachment of hydrophobic bacteria to oil droplets, making the process very complex to understand. The study concludes that no systematic and reproducible effects of chemical dispersion on the biodegradation rate of crude oil have been demonstrated. The study also notes the experimental systems used to investigate these effects might be inappropriate to represent the environment, because the systems applied high mixing energy in an enclosed, nutrient sufficient environment and allowed sufficient time for microbial growth. Microbial growth on open-ocean slicks is likely to be nutrient limited and may be slow relative to processes that lead to the formation of water-in-oil emulsions, which are resistant to biodegradation. It also noted that the most toxic components of the oil, the biodegradation of PAHs, have never been shown to be stimulated by dispersants.

2014 This study repeats some of the above conclusions but also summarizes results of these biodegradation studies 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.

3.3.1 Bacterial Population Shifts

Introduction

New studies have shown that when oil and dispersants are involved, especially dispersants, there is typically a shift in the population of microbes that degrade oil. This shift can be minor or can be very major. This shift has a strong influence on the amount of degradation that takes place and on the type of compounds that are degraded. For example, the population of alkane degraders may be increased or decreased and the population of PAH degraders may be altered in a different direction. Further, the natural successions that occur during biodegradation may be shifted or altered.

Summary and Conclusions

Several studies have shown that the presence of dispersants alters both the numbers and succession of hydrocarbon degrading organisms. This appears to be the result of selective toxicity of dispersants to some species while other species are tolerant of dispersants. This effect would be different for different dispersants and different dispersant constituents. The end result of this number and succession shift is generally a reduction in biodegradation compared to a situation where dispersants are not used. The other result is that certain components of oil are degraded faster or slower than they would be if dispersants were not used.

Detailed Study Summaries

Meng et al. (2016) studied structure shifts of bacterial compositions before, during and after crude oil exposure to determine the microbial response. Test of how temperature, dispersants and nutrients affect the composition of microbial communities or their activities of biodegradation in artificial marine environment were carried out. During petroleum hydrocarbons exposure, the composition and functional dynamics of marine microbial communities were altered, favoring bacteria that could utilize oil such as the Proteobacteria, Firmicutes, Actinobacteria and Bacteroidetes phyla. Low temperature decreased bacterial richness and catabolic diversity due to abated enzyme activity. Dispersants change bacterial composition by increasing the population of Chloroflexi, TM6, OP8, Cyanobacteria and Gemmatimonadetes phyla.

Al-Jawasim et al. (2015) found that a combined effect of crude oil plus dispersant (Corexit 9500A) significantly altered indigenous bacterial communities in a Louisiana salt marsh sediment after 30 days of incubation. The crude oil and/or Corexit 9500A treatments triggered shifts in bacterial communities and the shift by crude oil plus Corexit 9500A was considerably different from those by either crude oil or Corexit 9500A. However, the synergistic effect of crude oil plus Corexit 9500A was not observed after 7 days of incubation; the bacterial community was slightly shifted by Corexit 9500A and the crude oil did not trigger any bacterial community shift after 7 days of incubation. The major shift was seen after 30 days DNA sequencing data indicated that Chromobacterium species was enriched in the Corexit 9500A microcosms after 7 days of incubation, while Pseudomonas, Advenella, Acidocella and Dyella spp. were enriched after 30 days of incubation. Parvibaculum was a dominant species in the crude oil microcosms after 30 days of incubation. Rhodanobacter, Dyella and Frateuria spp. were dominant in crude oil plus Corexit 9500A microcosms after 30 days of incubation. The data show that the effect of crude oil plus Corexit 9500A on bacterial community is synergistic, and thus the dispersant effect should be considered with the spilled oil to evaluate the environmental impact.

Crisafi et al. (2016) investigated the effect of three treatments in oily-seawater after a real oil-spill in the Gulf of Taranto, Italy. Biostimulation with inorganic nutrients allowed the biodegradation of the 73 % of hydrocarbons, bioaugmentation with a selected hydrocarbonoclastic consortium consisting of *Alcanivorax borkumensis*, *Alcanivorax dieselolei*, *Marinobacter hydrocarbonoclasticus*, *Cycloclasticus sp. 78-ME* and *Thalassolituus oleivorans* degraded 79 %, while the addition of nutrients and a washing agent has allowed the degradation of the 69 %. On the other hand, microbial community was severely affected by the addition of the washing agent and the same product seemed to inhibit the growth of the majority of strains composing the selected consortium at the tested concentration. The use of dispersant should be accurately evaluated also considering its effect on the principal biodegradation species.

King et al. (2015a) discuss results of bacterial surveys following the Deepwater Horizon Spill which have shown an unexpectedly rapid response of deep-sea Gammaproteobacteria to oil and gas and documented a distinct succession correlated with the control of the oil flow and well shut-in. Similar successional events, also involving Gammaproteobacteria, have been observed in nearshore systems. The scientists note that no connection can be definitively drawn to these events and the use of dispersants.

Kleindienst et al. (2016a) observed an enrichment of distinct microbial populations after the DWH spill, noting that little is known about the abundance and richness of specific microbial ecotypes involved in gas, oil and dispersant biodegradation in the wake of oil spills. They document a previously unrecognized diversity of closely related taxa affiliating with Cycloclasticus, Colwellia and Oceanospirillaceae and describe their spatio-temporal distribution in the Gulf's Deepwater, in close proximity to the discharge site and at increasing distance from it, before, during and after the discharge. A highly sensitive, computational method (oligotyping) applied to a data set generated from 454-tag pyrosequencing of bacterial 16S ribosomal RNA gene V4-V6 regions, enabled the detection of population dynamics at the sub-operational taxonomic unit level (0.2% sequence similarity). The biogeochemical signature of the deep-sea samples was assessed via total cell counts, concentrations of short-chain alkanes (C1-C5), nutrients, dissolved organic and inorganic carbon, as well as methane oxidation rates. Statistical analysis elucidated environmental factors that shaped ecologically relevant dynamics of oligotypes, which likely represent distinct ecotypes. Major hydrocarbon degraders, adapted to the slow-diffusive natural hydrocarbon seepage in the Gulf of Mexico, appeared unable to cope with the conditions encountered during the DWH spill or were outcompeted. In contrast, diverse, rare taxa increased rapidly in abundance, underscoring the importance of specialized sub-populations and potential ecotypes during massive deep-sea oil discharges and perhaps other large-scale perturbations.

Kleindienst et. al. (2015) publish findings showing that the use of dispersants modifies the composition of the microbial community, often diminishing those of oleoclastic communities. These results are controversial, probably owing to variations in laboratory methods, the selected model organisms and the chemistry of different dispersant-oil mixtures. Here, they argue that an in-depth assessment of the impacts of dispersants on microorganisms is needed to evaluate the planning and use of dispersants during future responses to oil spills.

Kleindienst et al. (2016c) simulated environmental conditions comparable to the hydrocarbon-rich, 1,100 m deep plume that formed during the Deepwater Horizon discharge. The presence of dispersant significantly altered the microbial community composition through selection for potential dispersant-degrading Colwellia, which also bloomed in situ in Gulf deep waters during the discharge. In contrast, oil addition to Deepwater samples in the absence of dispersant stimulated growth of natural hydrocarbon-degrading Marinobacter. In these Deepwater microcosm experiments, dispersants did not enhance heterotrophic microbial activity or hydrocarbon oxidation rates. An experiment with surface seawater from an anthropogenically derived oil slick corroborated the Deepwater microcosm results as inhibition of hydrocarbon turnover was observed in the presence of dispersants, suggesting that the microcosm findings are broadly applicable across marine habitats. Extrapolating this comprehensive dataset to real world scenarios questions whether dispersants stimulate microbial oil degradation in deep ocean waters and instead highlights that dispersants can exert a negative effect on microbial hydrocarbon degradation rates.

Ortmann and Lu (2015) characterized the short-term response of coastal bacteria to dispersant, oil and dispersed oil using 16S rRNA gene tags in two mesocosm experiments conducted two months apart. Despite differences in the amounts of oil-derived alkanes across the treatments and experiments, increases in the contributions of hydrocarbon degrading taxa and decreases in common estuarine bacteria were observed in response to dispersant and/or oil. Between the two experiments, the direction and rates of changes in particulate alkane concentrations differed, as did the magnitude of the bacterial response to oil and/or dispersant. Together, the data underscore large variability in bacterial responses to hydrocarbon pollutants, implying that bioremediation success varies with starting biological and environmental conditions

Overholt et al. (2016) utilized two environmentally relevant species of hydrocarbon-degrading bacteria to quantify the response to Macondo crude oil and Corexit 9500A-dispersed oil in terms of bacterial growth and oil degradation potential. In addition, specific hydrocarbon compounds were quantified in the dissolved phase of the medium and linked to ecotoxicity using a U.S. Environmental Protection Agency-approved rotifer assay. Bacterial treatment significantly and drastically reduced the toxicity associated with dispersed oil (increasing the 50% lethal concentration [LC_{50}] by 215%). The growth and crude oil degradation potential of Acinetobacter were inhibited by Corexit by 34% and 40%, respectively; conversely, Corexit significantly enhanced the growth of Alcanivorax by 10% relative to that in undispersed oil. Furthermore, both bacterial strains were shown to grow with Corexit as the sole carbon and energy source. Hydrocarbon-degrading bacterial species demonstrate a unique response to dispersed oil compared to their response to crude oil, with potentially opposing effects on toxicity. While some species have the potential to enhance the toxicity of crude oil by producing biosurfactants, the same bacteria may reduce the toxicity associated with dispersed oil through degradation or sequestration.

Results from Previous Literature Reviews

This section or analysis did not appear in previous reviews.

3.4 Marine Snow Formation

Introduction

There are two types of marine snow: microbial-derived marine oil snow (MDOS): Produced by microorganisms as a by-product of oil biodegradation and phytoplankton-derived marine oil snow (PDOS): Phytoplankton exposed to oil increase production of Transparent Exopolymer Particles (TEP) as a protective mechanism. This TEP emulsifies oil and produces PDOS. The planktonic (microbial and phytoplankton) communities exposed to oil produce more TEP, which facilitates the formation of marine snow, which sinks as a result of flocculation processes and can scavenge other suspended materials in the water column. Both processes have been found to result in significant oil removal.

Summary and Conclusions

Marine snow production occurs during spills and is increased by the presence of dispersants. Marine snow results in the sedimentation of oil to the sea floor, where its fate is relatively unknown. Studies of past spills show that these spills precipitated increased amounts of marine snow. Studies of the Deepwater Horizon spill shows that as much as 14% of all the oil may have been sedimented to the sea floor as marine snow.

Detailed Study Summaries

Daley et al. (2016) summarize marine snow formation, incorporation of oil, and subsequent gravitational settling to the seafloor (i.e., MOSSFA: Marine Oil Snow Sedimentation and Flocculent Accumulation) was a significant pathway for the distribution and fate of oil in the case of the Deepwater Horizon, accounting for as much as 14% of the total oil released. Long residence times of oil on the seafloor will result in prolonged exposure by benthic organisms and economically important fish. Bioaccumulation of hydrocarbons into the food web also has been documented. Major surface processes governing the MOSSFA event included an elevated and extended Mississippi River discharge, which enhanced phytoplankton production and suspended particle concentrations, zooplankton grazing, and enhanced microbial mucus formation. Previous reports indicated that MOS sedimentation also occurred during the Tsesis and Ixtoc-I oil spills; thus, MOSSFA events may occur during future oil spills, particularly since 85% of global deep-water oil exploration sites are adjacent to deltaic systems. They provide a conceptual framework of MOSSFA processes and identify data gaps to help guide current research and to improve the ability to predict MOSSFA events under different environmental conditions.

Kinner et al. (2014) report on a town hall meeting where fate of DWH oil was discussed. Scientists from different research consortia studying sediments and marine snow in the Gulf began to observe signs of increased sedimentation and hydrocarbon deposition. Sediment mass accumulation rates for the northern Gulf of Mexico increased six-fold to eightfold in 2010, directly following the DWH blowout.

Passow (2016) noted that significant amounts of oil accumulated at the sea surface and in a subsurface plume during the Deepwater Horizon spill in the Gulf of Mexico. A substantial fraction of this oil was removed from the marine environment by mechanical recovery or burning, or it reached shorelines, whereas another fraction remained within the marine environment, where it dispersed (chemically or naturally), emulsified or sedimented. After the DwH accident the sedimentation of hydrocarbons to the seafloor via rapidly sinking, oil-associated marine snow has become a focus of attention, and it has been hypothesized that marine snow formation significantly impacted the distribution of the oil from the DwH spill. Roller table experiments are presented that investigated the conditions inducing the formation of oil-associated marine snow, focusing especially on the effects of oil type, photochemical aging of oil, and the presence of phytoplankton or dispersant. Large, mucus-rich marine snow, termed microbial marine snow, formed in treatments incubated with the oil that had accumulated at the sea surface. This bacteria-mediated formation of up to cm-sized marine snow in the absence of particles >1 μm, represents a unique formation pathway different from that of the physical coagulation of particles. Microbial marine snow, albeit smaller, also formed in the presence of crude oil that had been aged for ≥3 weeks in sunlight, but no particles formed in the presence of unaltered crude. The dispersant Corexit 9500A (Corexit:oil ratio=1:100) impeded the formation of microbial marine snow, requiring a re-evaluation of the benefits and detriments of Corexit 9500A as a mediating measure. Phytoplankton aggregates also incorporated fossil carbon, providing an alternate pathway for the formation of oil-associated marine snow. The ubiquitous formation and rapid sedimentation of oil-rich marine snow can explain the high accumulation rate of flocculent material at the seafloor and on corals observed after the DwH spill.

Passow and Ziervogel (2016) found that during and after the Deepwater Horizon (DWH) spill in the northern Gulf of Mexico, a massive amount of oil compounds and marine particles, termed floc, accumulated on the seafloor. It is now well established that sedimentation of oil following the DWH spill occurred largely in association with marine oil snow (MOS), a term that became accepted as describing marine snow that incorporates oil. A significant amount of the spilled oil made its way to the seafloor as MOS, appreciably affecting the distribution of oil within the ocean.

van Eenennaam et al. (2016) used two marine phytoplankton species (Dunaliella tertiolecta and Phaeodactylum tricornutum) to study marine snow formation. These phytoplankton produced EPS (Extracellular Polymeric Substances) or marine snow within days, when exposed to the dispersant Corexit 9500. Phytoplankton-associated bacteria were shown to be responsible for the formation. The EPS consisted of proteins and to lesser extent, polysaccharides. This study reveals an unexpected consequence of the presence of phytoplankton, emphasizing the need to test the action of dispersants under realistic field conditions, which may seriously alter the fate of oil in the environment via increased marine snow formation.

Vonk et al. (2015) note that during the Deepwater Horizon blowout, thick layers of oiled material were deposited on the deep seafloor. This large scale benthic concentration of oil is suggested to have occurred via the process of Marine Oil Snow Sedimentation and Flocculent Accumulation (MOSSFA). This meta-analysis investigates whether MOSSFA occurred in other large oil spills and identifies the main drivers of oil sedimentation. MOSSFA was found to have occurred during the IXTOC I blowout and possibly during the Santa Barbara blowout. Unfortunately, benthic effects were not sufficiently studied for the 52 spills reviewed. However, based on the current understanding of drivers involved, they conclude that MOSSFA and related benthic contamination may be widespread. They suggest to collect and analyze sediment cores at specific spill locations, as improved understanding of the MOSSFA process will allow better informed spill responses in the future, taking into account possible massive oil sedimentation and smothering of (deep) benthic ecosystems

Yan et al. (2016) showed that data from a deep sediment trap, deployed 7.4 km SW of the well between August 2010 and October 2011, revealed that the sinking of spill-associated substances, mediated by marine particles, especially phytoplankton, continued at least 5 months following the capping of the well. In August/September 2010, an exceptionally large diatom bloom sedimentation event coincided with elevated sinking rates of oil-derived hydrocarbons, black carbon, and two key components of drilling mud, barium and olefins. Barium remained in the water column for months and even entered pelagic food webs. Both saturated and polycyclic aromatic hydrocarbon source indicators corroborate a predominant contribution of crude oil to the sinking hydrocarbons. Co-sedimentation with diatoms accumulated contaminants that were dispersed in the water column and transported them downward, where they were concentrated into the upper centimeters of the seafloor, potentially leading to sustained impact on benthic ecosystems.

Results from Previous Literature Reviews

This topic did not appear in previous literature reviews.

3.5 Fate Impacted by Dispersant Use

Introduction

The use of dispersants may impact the fate of oil from a spill in ways not discussed above. This section reviews a few studies on this topic.

Summary and Conclusions

The studies under this category show that dispersants do increase the amount of BTEX into the water column as is already well known. Further, one study shows that dispersions also change the processes of fecal pellets in copepods by incorporating smaller oil droplets.

Detailed Study Summaries

Almeda et al. (2016b) investigated and quantified defecation rates of crude oil by 3 species of marine planktonic copepods (*Temora turbinata*, *Acartia tonsa*, and *Parvocalanus crassirostris*) and a natural copepod assemblage after exposure to mechanically or chemically dispersed crude oil. Between 88 and 100% of the analyzed fecal pellets from three species of copepods and a natural copepod assemblage exposed for 48 h to physically or chemically dispersed light crude oil contained crude oil droplets. Crude oil droplets inside fecal pellets were smaller (median diameter: 2.4-3.5 μm) than droplets in the physically and chemically dispersed oil emulsions (median diameter: 6.6 and 8.0 μm, respectively). This suggests that copepods can reject large crude oil droplets or that crude oil droplets are broken into smaller oil droplets before or during ingestion. Depending on the species and experimental treatments, crude oil defecation rates ranged from 5.3 to 245 ng-oil/copepod.d, which represent a mean weight-specific defecation rate of 0.026 μg-oil μg/copepod.d. Considering a dispersed crude oil concentration commonly found in the water column after oil spills (1 μL/L) and copepod abundances in high productive coastal areas, copepods may defecate ∼1.3-2.6 mg-oil m^{-3} d^{-1}, which would represent ∼0.15%-0.30% of the total dispersed oil per day. The results indicate that ingestion and subsequent defecation of crude oil by planktonic copepods has a small influence on the overall mass of oil spills in the short term, but may be quantitatively important in the flux of oil from surface water to sediments and in the transfer of low-solubility, toxic petroleum hydrocarbons into food webs after crude oil spills.

Simpson et al. (2015) describe a laboratory experiment to introduce environmental NMR spectroscopy to upper-level undergraduate and graduate students in a simple and accessible manner. Students investigate the partitioning of crude oil components into water under various environmental conditions; assess the effects of agitation and dispersants on dissolution; and identify benzene, toluene, ethylbenzene, and xylene components through standard addition. This educational demonstration shows how BTEX is very much increased in the water column by the use of dispersants.

4 Other Issues

4.1 Dispersant Use in Recent Times and NEBA

Introduction

Dispersant use in recent times has been dominated by the extensive use of dispersants at the Deepwater Horizon spill. There have been few reports of use outside this incident.

Further, use in recent time is dominated by net environmental benefit analysis (NEBA) (Alekseevna and Seryy, 2015; Irving and Lee, 2015). This is a system of considerations for dispersant use including the effect of not using them. Much of the discussion is about past issues, particularly the Deepwater Horizon incident and use of dispersants there.

Summary and Conclusions

Much of the discussion still revolves around the use of dispersants during the Deepwater Horizon spill. Re-evaluation of this spill notes that neither sub-sea nor on-sea dispersion was evaluated for effectiveness and thus discussion will continue on how effective these applications really were. This is especially true, considering the large amounts of oil observed to have impacted the shoreline and to have sedimented to the seafloor.

Focus on dispersant use continues on using NEBA or Net Environmental Benefit Analysis and good communication with stakeholders.

Detailed Study Summaries

Belkina et al. (2015) review the “Joint Contingency Plan in the Barents Sea” and any specific requirements for use of dispersants. The plan emphasizes that in case of transboundary pollution the decision to use dispersants shall only be undertaken upon common agreement. The paper presents a comparison of the national regulatory approaches of Norway and Russia to using dispersants. The research is based on the analysis of legislative documents and interviews with oil companies, oil spill responders and relevant national authorities. The research reveals that in both countries use of dispersants requires preliminary authorization of the national agencies. In Norway, the pre-approval procedure and the algorithm of dispersants involvement in response to a real accident are clearly documented and are regularly tested. This has made the process of approval for using dispersants more efficient. In Russia, the lack of practical experience in using dispersants and well-established approval procedures can result in a long and unclear permitting process for each oil spill case. This could seriously hinder the use of dispersants to combat transboundary pollution in the Barents Sea, even if it is considered to be beneficial.

Bostrom et al. (2015) carried out a survey regarding oil spills. The study uses qualitative interview results and a response risk decision model to the design of a survey instrument. The decision model considers controlled burning, public health, and seafood safety. Surveying U.S. coastal residents (36,978 pairs of responses) through Google Insights identifies beliefs and gaps in understanding as well as related values and preferences about oil spills, and oil spill responses. A majority of respondents are concerned about economic impacts of major oil spills, and tend to see ocean ecosystems as fragile. They tend to see information about chemical dispersants as more important than ecological baseline information, and dispersants as toxic, persistent, and less effective than other response options. Although respondents regard laboratory studies as predictive of the effects of oil and of controlled burning, they are less confident that scientists agree on the toxicity and effectiveness of dispersants. Similarly, Dailey and Starbird (2015) discuss decision-making in the case of crisis situations noting the difficulty of decision-making in times of crisis.

Fingas (2017) reviews the mass balance of the DWH spill noting that the blowout from the Macondo well has led to much discussion on the fate of the oil. There are a number of studies of the oil fate conducted in the past few years. Since an early study on mass balance, much new information has come forward on oil weathering, fates in the sea, skimming and oil on the shoreline. This re-evaluation focusses on the amounts that are readily measured or estimated. The methodology used in this paper was to use literature values or estimation where necessary. The amount of oil released by the blowout was estimated to be 578,000 m^3 (3,635,000 barrels). The amount of oil surfaced is estimated to be about 50% of the oil released. On the surface, skimming removed an estimated 34%, the amount on shore accounted for 19%, burning removed 15%, and weathering accounted for an amount of 11%. The amount of sunken oil and that deposited as marine snow was estimated to be 7%. Oil that moved out of the area was estimated to be 3% and various other fates accounted for 3%. The fate of 6% of the oil is unknown. In the subsurface, fate of the oil was estimated to be dominated by dissolution, 28%, and dispersion in and out of plumes, 18% for each. Marine snow and sedimentation accounted for another 13%, while the fate of about 24% of the oil was unknown. The largest amount of error in this study, is in the estimation of the fate of the subsea oil. On the surface, the amount of oiled shoreline has the largest estimation variances. The remaining variances are generally within 10% of the individual component. A time analysis of the oil on the surface compared to the estimations carried out in this study and compared to remote sensing measurements shows agreement. This comparison shows that the major influences on the amounts of surface oil were the skimming, shoreline encounter and burning. Further influences were the necessary mobilization times, the siphoning of oil from the well over a period of 10 days, Hurricane Alex and the incumbent demobilization of equipment from the sea.

MacDonald et al. (2015) applied neural network analysis of satellite SAR images to quantify the magnitude and distribution of surface oil in the Gulf of Mexico from persistent, natural seeps and from the Deepwater Horizon (DWH) discharge. This analysis identified 914 natural oil seep zones across the entire Gulf of Mexico in pre-2010 data. Their ~0.1 μm slicks covered an aggregated average of 775 km^2. Assuming an average volume of 77.5 m^3 over an 8-24 h lifespan per oil slick, the floating oil indicates a surface flux of 2.5-9.4 × 104 m^3 yr^{-1}. Oil from natural slicks was regionally concentrated: 68%, 25%, 7%, and <1% of the total was observed in the NW, SW, NE, and SE Gulf, respectively. SAR images from 2010 showed that the 87-day DWH discharge produced a surface-oil footprint fundamentally different from background seepage, with an average ocean area of 11,200 km^2 and a volume of 22,600 m^3. Peak magnitudes of oil were detected during equivalent, ~14 day intervals around 23 May and 18 June, when wind speeds remained <5 m s^{-1}. Over this interval, aggregated volume of floating oil decreased by 21%; area covered increased by 49%, potentially altering its ecological impact. The most likely causes were increased application of countermeasures.

McDaniel et al. (2015) suggest oil from the DWH spill could have contaminated the West Florida Shelf (WFS). They utilized polycyclic aromatic hydrocarbon (PAH) analysis to determine presence and potential origin of oil contaminants in beach sand patty samples. PAH profiles from

WFS beaches were statistically significantly similar to DWH contaminated samples from the Northeast Gulf of Mexico (Gulf Shores, AL; Ft. Pickens, FL). Dioctyl sodium sulfosuccinate (DOSS), a major component of Corexit 9500 dispersant was also detected in the sediments. DOSS concentrations ranged from 1.6 to 5.5 ngg^{-1} dry weight. Additionally, two samples from DWH oil contaminated beaches were acutely toxic and one WFS beach sediment sample was mutagenic. These observations provide support for the theory that DWH oil made its way onto beaches of the WFS.

Rudder et al. (2015) examine the response measures utilized during the multiple oil spills of December 2013 in Trinidad. In addition, it will explore how successful these response measures were, the adjustments that were made, the challenges with public relations and other factors that negatively impacted the response. Also, a discussion of what technological features would have improved the actual responses to the multiple oil spills with particular reference to the La Brea Oil Spill. Managing the response to this La Brea spill necessitated the use of the Incident Command System (ICS) as required under the NOSCP as well as the activation of the NOSCP to the Tier 3 level. A variety of response equipment and resources such as booms, dispersants, degreasers and shoreline cleaners as well as vessel and aerial surveillance were utilized. The decision to utilize Corexit 9500A in the response elicited national condemnation. In addition, the fact that mangroves were impacted by oil and they were purposely not cleaned received condemnation. There was major dissatisfaction with the mechanisms employed to conduct beach cleaning which prolonged the clean-up. The spill caused disgruntlement amongst the affected residents.

Venosa et al. (2014) summarize the perspectives in use of dispersants during the DWH spill response.

Walker et al. (2015) review public engagement through both traditional and social media which was arguably much higher than in prior spills. The DWH response organization undertook a wide variety of activities to manage risks and communicate with both the general public and those directly affected, such as commercial fishers. However, these did not fully address widespread concerns about ecological and human health risks associated with dispersant use. Consequentially the DWH spill heightened awareness of persistent risk communication problems around oil spill response, and especially dispersant use. Oil spill risk research and experience suggests that institutional and operational factors inhibit engaging communities and stakeholders during oil spill preparedness and response, and that such engagement is essential for effective risk management. They review and assess current oil spill preparedness and response practices for community and stakeholder engagement, including related institutional and operational constraints. This assessment suggests five example risk management practices to improve and advance risk communications during oil spill preparedness and response activities.

Results from Previous Literature Reviews

2002 There are no new descriptions in the literature of operations directly relevant to dispersant use in Alaska. There have been three small applications of dispersant in the Gulf of Mexico. It should be noted, however, that oil is highly dispersible and the water temperatures much higher in the Gulf of Mexico. There are no cold-water dispersant applications described in the literature. Only one dispersant application other than those in the Gulf was noted in the world, that of the

Sea Empress in Britain. In this case, dispersants were applied from DC-3 and Hercules aircraft over a part of the slick. Mass balance calculations indicated a loss of oil, although there was extensive coastal oiling. Policies concerning dispersants in other parts of the world have not changed significantly since the last report. In Europe, only Britain uses dispersants extensively, although they may be used in Norway and France. No documented use of dispersants has been found in any European country except for the *Sea Empress* case noted throughout this report. The Baltic countries do not use dispersants and laws against their use are found nationally and internationally in the HELCOM treaties. In North America, several states in the U.S. have moved to allow dispersant use, but dispersants have only been used three times, all of them in the Gulf of Mexico.

2008 Dispersant use in recent times is not well-documented or is in fact, decreasing. Scientific assessment of dispersant effectiveness at spill scenes is often not carried out.

2014 Dispersant use in recent times was 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.

4. 2 Monitoring Dispersant Effectiveness

Introduction

An important part of dispersant application is the measurement of the initial effectiveness of the application. For about 2 decades, this was done with SMART - Special Monitoring of Applied Response Technologies. These protocols have not been updated for many years and many felt that there were flaws in the protocols and certainly improvements that could be made.

Summary and Conclusions

New dispersant effectiveness monitoring protocols have been suggested and published. These include the following advances: use of a field effectiveness test to pre-screen slicks for effectiveness; new guidelines for visual observation of effectiveness along with times; use of modern instruments that measure particle size and also can integrate these into total oil measurements; sampling and analysis of water below slicks; and shipboard toxicity measurements.

Detailed Study Summaries

PWS RCAC (2016) summarized a proposed new monitoring protocol to monitor dispersant application for effectiveness. Suggestions for improvements by the many parties who carried out monitoring work on the Deepwater Horizon are incorporated and new concepts advanced to address these suggestions. The primary decision point for making dispersant applications on a particular day is proposed to be a simple field test. This field test involves a simple method with four repetitions. The other protocols are suggested to be in three ‘levels’. Level 1 is an important level involving visual monitoring from an aircraft over the slick. Photographs of effective and not effective dispersant applications are given as a guide. Instructions and points-to-note for this level are given. Level 2 involves towing instruments through the un-dispersed and dispersed slicks at depths of 2 and 5 m. The tow consists of a LISST-100X particle instrument which has an onboard fluorometer (Turner Cyclops-7) and an Aqua Monitor, which is a towed water sampler. A depth meter provides confirmation of sampling depth. The data from the LISST includes an integrated particle count, similar to a Total Petroleum Hydrocarbon (TPH) measurement, and a Volume Mean Diameter (VMD). It is proposed that an effective dispersion results if the integrated particle count (TPH) measurement is at least 10 times the background value and that the VMD is less than 50 µm over a large part of the sample tow. The output of the fluorometer can give confirmation that the particles are oil or not. Water samples are analyzed in the laboratory for TPH and TPAH to confirm field readings. The results of these readings on a particular day and a new field test in the morning would form the basis for a decision for the day's dispersant application. There is Level 3 which consists of taking water samples for further analysis by two different methods. One is using the Payne sampler which provides a separation between particulate and dissolved material. These two samples are analyzed in the laboratory for TPH and TPAH and specific compounds if so desired. Another sample is taken at 2 m and optionally at 5 m using an Alpha sampler. This sample is split into 3 samples, two 1000 mL samples, one for chemical analysis and the other for laboratory toxicity studies. A third smaller split of about 200 mL is used for onboard MicroTox assessment. Several alternate laboratory analyses are also summarized. The improvements over the previous protocols include the use of particle measurement as an indicator of effectiveness rather than fluorescence; the inclusion of a field effectiveness test and use of a towed sampling device.

Qi et al. (2015) new monitoring kit to measure dispersant field effectiveness. This kit contains multiple channels of chemical sensors. It is capable of providing in situ monitoring of property change of chemically dispersed oil in addition to overall increase of dispersed oil in water and therefore can yield more quantitative assessment of oil dispersant effectiveness. The towed platform that the sensors are mounted on has the unique flexibility to be deployed in two different modes for fixed depth (~1 m) subsurface water monitoring and water column profiling respectively.

Svejkovsky et al. (2016) utilized very high resolution (≤ 5 m) aerial and satellite imagery acquired during the DWH spill to evaluate the shape, size and thickness of surface oil features. Results indicate that outside of the immediate spill source region, oil distributions did not encompass a broad, varied range of thicknesses. Instead, the oil separated into four primary, distinct characterizations: 1) invisible surface films detectable only with Synthetic Aperture Radar imaging because of the decreased surface backscatter, 2) thicker sheen and rainbow areas (< 0.005 mm), 3) large regional areas of relatively thin, "metallic appearance" films (0.005–0.08 mm), and 4) strands of thick, emulsified oil (> 1 mm) that were consistently hundreds of meters long but most commonly only 10–50 m wide. Where present within the slick footprint, each of the three distinct visible oil thickness classes maintained its shape characteristics both spatially (at different distances from the source and in different portions of the slick), and temporally (from mid-May through July 2010). The region over the source site tended to contain a more continuous range of oil thicknesses, however, their results indicate that the continuous injection of subsurface dispersants starting in late May significantly altered (lowered) that range.

Results from Previous Literature Reviews

2008 The purpose of monitoring is to determine if a dispersant application was relatively effective or not; to provide information to the responders and to provide scientific information for decision-making and modeling. The most common protocol now is the SMART monitoring protocol from a number of USA government agencies. The protocols currently consist of some visual criteria and often include a sub-surface monitoring program consisting of using in-situ fluorometers to gauge the relative effectiveness of a dispersant application. It should be noted that there are no monitoring guidelines in SMART or many other protocols. Some types of biological monitoring, it is felt, are needed. There are many false positives and false negatives with both monitoring techniques. These can be overcome by paying attention to the science and technology. Monitoring by visual or fluorometer means can only yield an estimate of the relative effectiveness of a dispersant application. Specifically, the monitoring produces an estimate of whether the effectiveness of an application is ineffective or somewhat effective. There are more methods described in the literature that can yield more information. It is recommended that a screening test of the dispersant effectiveness be carried out before any test application of the dispersant. This test should show a dispersion of about one-half of the oil. It is suggested that the prime monitoring technique for actual dispersant application is visual. Extensive work is required to produce visual monitoring guidelines and visual aids. It was also pointed out that monitoring of oil concentrations in the water column would provide useful scientific information. This information may not be useful to the incident commanders, however, because of the complexities of the measurements and the timing of the analytical results. Because such concentration information is necessary for future science, good measurements should be taken if at all possible. In summary, effectiveness monitoring at actual dispersant operations could provide very useful information for future assessment, modeling and basic understanding of chemical dispersion. Emphasis must be placed on obtaining accurate and precise data.

2014 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 are 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

Introduction 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. 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.

Summary and Conclusions

Several studies continued on oil-sediment interaction. Results are conclusive that dispersants increase the amount of oil-sediment aggregates formed as a result of the more droplets of oil in the water column. Increasing the sediment content in a dispersion, also increases the total amount dispersed. The mineral aggregates thus formed will sediment to the bottom, given time and quiescence. There are variabilities in these processes with temperature, oil type, oil viscosity and oil weathering.

Detailed Study Summaries

Bodratti et al. (2014) show that the addition of surfactants increases the oil-mineral interactions resulting in more sedimentation.

Boglaienko and Tansel, (2016) analyzed the phase distribution of fresh floating Louisiana crude oil into dispersed, settled and floating phases depending on the exposure sequence to Corexit 9500A (dispersant) and granular materials. In artificial sea water at salinity 34‰. Limestone (2.00-0.300 mm) and quartz sand (0.300-0.075 mm) were used as the natural granular materials. Dispersant Corexit 9500A increased the amount of dispersed oil up to 33.76%. Addition of granular materials after the dispersant increased dispersion of oil to 47.96 %. When solid particles were applied on the floating oil before the dispersant, oil was captured as oil-particle aggregates and removed from the floating layer. However, dispersant addition led to partial release of the captured oil, removing it from the aggregate to the dispersed and floating phases. There was no visible oil aggregation with the granular materials when quartz or limestone was at the bottom of the flask before the addition of oil and dispersant. The results show that granular materials can be effective when applied from the surface for aggregating or dispersing oil. However, the granular materials in the sediments are not effective neither for aggregating nor dispersing floating oil.

Burns and Jones (2016) assess the sediment contamination from the blowout of the Montara H1 well (August, 2009) 260 km off the northwest coast of Australia resulting in the release of about 4.7 M L of light crude oil and gaseous hydrocarbons into the Timor Sea. Over the 74-day period of the spill, the oil remained offshore and did not result in shoreline incidents on the Australia mainland. At various times slicks were sighted over a 90,000 km^2 area, forming a layer of oil which was tracked by airplanes and satellites but the slicks typically remained within 35 km of the well head platform and were treated with 183,000 L of dispersants. The shelf area where the spill occurred is shallow (100-200 m) and includes off shore emergent reefs and cays and submerged banks and shoals. This study describes the increased inputs of oil to the system and assesses the environmental impact. Concentrations of hydrocarbon in the sediment at the time of survey were very low (total aromatic hydrocarbons (PAHs) ranged from 0.04 to 31 ng g-1) and were orders of magnitude lower than concentrations at which biological effects would be expected. The relation between dispersant use and sedimentation was dealt with.

Cai et al. (2017) investigated effects of three oil dispersants (Corexit EC9527A, Corexit EC9500A and SPC1000) on the settling of fine sediment particles and particle-facilitated distribution and transport of oil components in sediment-seawater systems. All three dispersants enhanced settling of sediment particles. The nonionic surfactants (Tween 80 and Tween 85) play key roles in promoting particle aggregation. The effects varied with environmental factors (pH, salinity, DOM, and temperature). The strongest dispersant effect was observed at neutral or alkaline pH and in salinity range of 0–3.5 wt%. The presence of water accommodated oil and dispersed oil accelerated settling of the particles. Total petroleum hydrocarbons in the sediment phase were increased from 6.9% to 90.1% in the presence of Corexit EC9527A, and from 11.4% to 86.7% for PAHs.

Gupta et al. (2014) discuss adsorption of suspended particles to the interface of surfactant-dispersed oil droplets altering emulsion phase and sedimentation behavior. This work examined the effects of model mineral aggregates (silica nanoparticle aggregates or SNAs) on the behavior of oil (octane)-water emulsions prepared using sodium bis(2-ethylhexyl) sulfosuccinate (DOSS). Experiments were conducted at different SNA hydrophobicities in deionized and synthetic seawater (SSW), and at 0.5. mM and 2.5. mM DOSS. SNAs were characterized by thermogravimetric analysis (TGA) and dynamic light scattering (DLS), and the emulsions were examined by optical and cryogenic scanning electron microscopy. In deionized water, oil-in-water emulsions were formed with DOSS and the SNAs did not adhere to the droplets or alter emulsion behavior. In SSW, water-in-oil emulsions were formed with DOSS and SNA-DOSS binding through cation-bridging led to phase inversion to oil-in-water emulsions. Droplet oil-mineral aggregates (OMAs) were observed for hydrophilic SNAs, while hydrophobic SNAs yielded quickly-sedimenting agglomerated OMAs.

Gustitus et al. (2017) identified two conflicting hypotheses in the literature: OMA formation 1) increases with weathering as a result of increased asphaltene and polar compound content; or 2) decreases with weathering as a result of increased viscosity. While it is indeed true that the viscosity and the relative amounts of polar compounds will increase with weathering, their net effects on OMA formation is unclear. Controlled laboratory experiments were carried out to systematically test these two conflicting hypotheses. Experimental results using light, intermediate, and heavy crude oils, each at five weathering stages, show a decrease in OMA formation as oil weathers, showing that hypothesis 2) is correct.

King et al. (2015c) used Cold Lake Blend (CLB) diluted bitumen (Dilbit) to evaluate the fate and transport of pre-weathered (6.2% w/w) Dilbit under environmental conditions both in spring (seawater temperature 8.5°C°C and salinity 27.7 practical salinity units [psu]) and in summer (seawater temperature 17.0°C and salinity 26.8 psu). The following oil spill treatments were considered: no treatment, dispersant alone, mineral fines (MF) alone, and dispersant plus MF. The aim was to determine their influences on the fate of spilled CLB at sea. When dispersant alone was used, the highest dispersion effectiveness (DE) was noted, and DE ranged from 45% to

59% under the selected environmental conditions. With no treatment and treatment of MF alone, CLB DE was insufficient under tested conditions. Total petroleum hydrocarbon (TPH) concentration in the water column was highest for the dispersant alone, followed by that of dispersant plus MF. TPH concentration for the dispersant alone increased abruptly with time. Droplet size distribution (DSD) resulting from dispersant alone had a unimodal shape, which was different than previously observed when conventional oils were treated with the dispersant. Cases of dispersant plus MF were thus characterized by a broader DSD compared with dispersant only and a gradual increase in TPH concentration.

Loh et al. (2014) and Loh and Yim (2016) review oil suspended particulate matter (SPM) aggregates (OSA) which are naturally occurring phenomena where oil droplets and particles interact to form aggregates. This aggregation could aid cleanup processes of oil contaminated waters or complicate matters by sedimentation. When OSA is formed, it makes oil less adhesive and would facilitate the dispersion of oil into the water column. Increased oil-water surface contact by OSA formation may enhance biodegradation of oil. Its applicability as a natural oil clean-up mechanism has been effectively demonstrated over past decades. There are many factors affecting the formation of OSA and its stability in the natural environment that need to be understood.

Rios et al. (2017) collected oil and sediment samples from Campos Basin and six stations of Paraguaçu estuary, Todos os Santos Bay, Brazil, to study oil-sediment interaction. The sediments samples were analyzed for organic matter determined by the EMBRAPA method, nitrogen determined by the Kjeldahl method, and phosphorus determined by the method described by Aspila. The oil trapped in OSA was extracted following the method described by Moreira. The experiment showed a relationship between the amount of organic matter and OSA formation and consequently the dispersion of the studied oil. On the basis of the buoyancy of OSA and the ecotoxicological effects on pelagic and benthic community, the priority areas for application of remediation techniques were Cachoeira, Maragogipe, and Salinas da Margarida because of the large amount of oil that accumulated at the bottom of the experiment flask (5.85%, 27.95%, and 38,98%; 4.2%, 17.66%, and 32.64%; and 11.82%, 8.07%, and 10.91% respectively).

Silva et al. (2015) study oil-suspended particulate matter aggregate (OSA) resulting from the interaction of droplets of dispersed oil in a water column and particulate matter. This structure reduces the adhesion of oil on solid surfaces, promotes dispersion, and may accelerate degradation processes. The effects of the addition of fine sediments (clay + silt) on the formation of OSA, their impact on the dispersion and degradation of the oil, and their potential use in recovering reflective sandy beaches were evaluated in a mesoscale simulation model. Two simulations were performed (21 days), in the absence and presence of fine sediments, with four units in each simulation using oil from the Recôncavo Basin. The results showed that the use of fine sediment increased the dispersion of the oil in the water column up to four times in relation to the sandy sediment. There was no evidence of the transport of hydrocarbons in bottom sediments associated with fine sediments that would have accelerated the dispersion and degradation rates of the oil. Most of the OSA that formed in this process remained in the water column, where the degradation processes were more effective. Over the 21 days of simulation, they observed a 40 % reduction on average of the levels of saturated hydrocarbons staining the surface oil.

Sun et al. (2014) studied the effect of level and duration of mixing energy on OSA formation using the standard reference material 1941b and Arabian light crude oil. The results showed that dispersed small oil droplets increased with an increase of both the level and duration of mixing energy to form multi-droplet OSAs. The sizes of the dispersed droplets varied between 5 and 10 μm under different conditions studied. The maximum oil trapping efficiency increased from 23% to 33%, the oil to sediment ratio increased from 0.30 to 0.43 g oil/g sediment, and the required shaking time decreased from 2.3 to 1.1 h as the shaking rate increased from 2.0 to 2.3 Hz. Based on the size measurement results, a breakage effect on the formed OSAs and sediment flocs was confirmed under high mixing energy level.

Zhao et al. (2016) examined the effects of model oil dispersants on dispersion, sorption and photodegradation of petroleum hydrocarbons in simulated marine and sediment systems. Three dispersants (Corexit 9500A, Corexit 9527A and SPC 1000) were used to prepare dispersed water accommodated oil (DWAO). Corexit 9500A preferentially dispersed C11–C20 n-alkanes, whereas Corexit 9527A was more favorable for smaller alkanes (C10–C16), and SPC 1000 for C12–C28 n-alkanes. Sorption of petroleum hydrocarbons on sediment was proportional to TPH types/fractions in the DWAOs. Addition of 18 mg/L of Corexit 9500A increased sediment uptake of 2–3 ring PAHs, while higher dispersant doses reduced the uptake. Both dispersed n-alkanes and PAHs were susceptible to photodegradation under simulated sunlight. For PAHs, both photodegradation and photo-enhanced alkylation were concurrently taking place.

Results from Previous Literature Reviews

2008 The interaction of droplets, particularly chemically-dispersed droplets appear 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.

2014 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. 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

Introduction

The basic physics and chemistry of oil droplets in water states that these have limited stability and will rise slowly to the surface, depending on droplet size. There are several de-stabilization processes at play in de-stabilizing such oil droplets.

Summary and Conclusions

Consideration of water-in-oil dispersion stability is an important matter. It is known that oil spill dispersions are sometimes temporary and re-surfaced slicks can appear. Further the amount of oil entering the water has been shown to be highly variable and this has also been observed to be related to the oil properties and the sea energy. An important facet of the problem is the slow rise and coalescence of droplets to the surface after dispersion. 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. 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.

Detailed Study Summaries

Wang et al. (2015b) studied the separation characteristics of an oil spill dispersant (OSD) and the oil were investigated, and the stability of the effect of the OSD was also studied. Firstly, the mixture of the oil and the OSD which have been poured into the seawater was thoroughly stirred, left to stand and observed. Later, the greatest separation degree with the oil and the final stability of the OSD was obtained through the analysis. Then, the stability of the combination between the oil and the OSD was studied under the conditions of no wave, intermittent wave and continuous wave. The study shows the OSD will gradually move away from the oil, which is influenced by the time and duration of the wave action.

Wang et al. (2015c) conducted stability studies and the results show the OSD will gradually move away from the oil, and the quantity and speed of the removed OSD is influenced by the intensity and duration of the wave action. The stability mechanism of the OSD effect is proposed in this study.

Zhuang et al. (2015) investigated the adsorption and desorption behaviors of dissolved petroleum hydrocarbons (DPHs) in a seawater-sediment system. Tidal flat sediment was used as the adsorbent, and crude oil was used as the adsorbate. The processes of adsorption and desorption at low concentration (<14.3 mg L-1) were described by the first-order kinetics model. The rate of desorption was slower than that of adsorption, and about 49% of the DPHs remained on the sediment. Therefore, the potential risk of pollution would exist for a long time. The adsorption isotherms could be better fitted to the linear isotherm model than the Freundlich and Langmuir models. The adsorption process is a physical adsorption, because ΔH was 39.0 kJ mol-1 which is less than 42.0 kJ mol-1. The change in n-alkanes in the process was more obvious than the aromatics; the weathering loss rate was 25.56%, the emulsification loss rate of the dispersant was 0.65% and the microbial degradation rate was 15.46%. The results showed the degradation processes of petroleum hydrocarbons in tidal flats.

Results from Previous Literature Reviews

2008 The literature confirms the well-known phenomenon that chemically-dispersed oil, as all oil-in-water emulsions, destabilizes after the initial dispersion. The destabilization of oil-in-water emulsions such as chemical oil dispersions is a consequence of the fact that most emulsions are not thermodynamically stable. Ultimately, natural forces move the emulsions to a stable state, which consists of separated oil and water. The rate at which this occurs is important. An emulsion that stays sufficiently stable until long past its practical use consideration may be said to be kinetically stable. Kinetic stability is a consideration when describing an emulsion. An emulsion is said to be kinetically stable when significant separation (usually considered to be half or 50% of the dispersed phase) occurs outside of the usable time. There are several forces and processes that result in the destabilization and resurfacing of oil-in-water emulsions such as chemically dispersed oils. These include gravitational forces, surfactant interchange with water and subsequent loss of surfactant to the water column, creaming, coalescence, flocculation, Ostwald ripening, and sedimentation.

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

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

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

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

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

Another important phenomenon when considering the stability of dispersed oil is the absorption/desorption of surfactant from the oil/water interface. This process is stated to be the most important process for chemical considerations of surfactants and interfacial chemistry. When surfactants are dissolved in a bulk phase such as water, they start to be absorbed at the oil surface or interface. The system moves toward equilibrium, that is equilibrium amounts of surfactant at the interface and in the bulk phase. Desorption occurs primarily as a result of the lower concentration of surfactants in the bulk phase or water. The surfactants will transfer back and forth from the oil/water interface until an equilibrium of concentration is established in the interface or in the bulk liquid (water). It is well known that in dilute solutions, much of the surfactant in the dispersed droplets ultimately partitions to the water column and thus is lost to the dispersion process. Little, if any, surfactant would partition back into the droplet in a dilute solution, which is the case for oil dispersions at sea. This is one important difference between dilute and concentrated solutions. 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, most researchers, recognize 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

Introduction

Fingas (2014) 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.

There are no new studies on this at this time.

4.6 Sub-surface Application and Subsurface Behavior

Introduction The Deepwater Horizon study was marked by the used of dispersants injected at the well head. Studies continue on the effectiveness and results of such a technique.

Summary and Conclusions

While studies on the results of deep-sea injection of dispersants did occur, especially the effect on droplet size, no directly-simulative studies have been carried out. Modeling or scale studies remain as the only means to address the questions. The results vary and to date there has been no definitive answer if the injection of dispersants during the Deepwater Horizon reduced droplet size or had any other effect.

Detailed Study Summaries

Brandvik et al. (2016a) investigated other ways of reducing the effects of interfacial tension, other than use dispersants within a subsea oil plume, such as increasing the interfacial shear by introducing more turbulence within the rising oil plume. Using a combination of laboratory experimentation and computational fluid dynamics (CFD) they have explored the potential of three mechanisms-1) a rotating bladed shearing mixer, 2) ultrasonic cavitation and 3) high pressure water jetting. Physical experiments were conducted at the SINTEF Tower Basin facility in Norway. A scaled-down oil plume of Oseberg blend (1 L/min) was subjected to shear using commercially available rotating and ultrasonic devices both normally supplied for industrial mixing applications and adapted for operation within the tank. Results were compared to chemically dispersed oil under the same conditions. CFD modelling of water jetting was conducted using the BP High Performance Computer facility adopting a Volume of Fluid (VOF) multiphase model with advanced turbulence modelling and automated mesh refinement. Boundary conditions were set to replicate, as close as practical, the dimensions and physical properties used in the tank experiments. Results indicate that all three modes of increasing interfacial shear could be effective in dispersing oil. The ultrasonic device created a broad distribution of oil droplet sizes, spanning 10-100 μm in diameter whilst the mechanical shearing technique dispersed oil droplets into a narrower size distribution, centered on 16 μm. These values fall close to the droplet size of 70 μm dispersed using chemicals. Estimation of droplet sizes in the water jetting scenarios yielded values <50 μm. These tank scale experiments indicate that a new class of oil spill response technology may be possible using a mechanical device-Subsea Mechanical Dispersion.

Brandvik et al. (2016b) present data from a comprehensive set of laboratory experiments to evaluate the formation, fate, and transition of dispersed oil droplets in the water column during a subsea oil and gas blowout in combination with subsea dispersant injection. Many sub-sea well blowout oil and gas release scenarios form relatively large oil droplets (multiple millimeters), which then rapidly rise through the water column to form thick slicks on the ocean surface, potentially very near the source. On the other hand, smaller oil droplets (500 microns) rise more slowly and can stay suspended in the water column for days to weeks. Dispersant injection is therefore suggested to reduce the potential for floating oil and associated volatile hydrocarbons that may threaten worker health and safety, and reach ecologically and economically sensitive surface water and shoreline environments. The oil that disperses into the water column may pose temporary elevated exposures to organisms in the immediate area, but research and experience has shown that those exposures are rapidly mitigated by the effects of dilution and microbial degradation of the dispersed oil. The results of the laboratory studies, which examined the influence of different variables on the initial oil droplet size in an oil release scenario including oil release velocity, dispersant dosage, dispersant injection method, oil temperature, high pressure, gas-to-oil ratio, oil- and dispersant characteristics), revealed that dispersant injection is highly effective at reducing droplet size. The data also fit a new modified Weber Number scaling algorithm that can be used to calculate initial oil droplet size at field scales. Model simulations using the new modified Weber number scaling indicate that subsea dispersant injection can reduce droplet size by an order of magnitude which serves to delay and significantly reduce surfacing of oil from large oil spills.

Broje et al. (2016) review oil spill response strategies for offshore spills including well control, natural attenuation, remote sensing, mechanical on-water recovery, dispersants used at the surface or subsea, in-situ burning, as well as shoreline protection and recovery. For offshore subsea releases, injection of dispersants subsea at a wellhead may offer significant benefits, including access to the freshest and non-emulsified oil in a high turbulence environment, ability to reduce the volume of required dispersant by injecting it directly into the oil stream, ability to safely operate day and night under a much wider range of weather conditions, and availability of a large water volume to rapidly decrease the concentration of a dispersed oil plume. To advance the science of subsea dispersant injection and provide a strong basis for inclusion of this technique into contingency plans the American Petroleum Institute (API) has sponsored research on various aspects of subsea dispersant injection for over 4 years. This comprehensive effort included studies on subsea dispersant injection effectiveness, oil fate and effects, subsea plume monitoring, and numerical modeling. Chopra and Coolbaugh (2016) also review some of these developments.

The U.S. National Research Council committee (2014) reviewed the subsea application and noted that the net environmental benefits or significant benefits of subsea dispersant application were not measured and would be difficult to establish.

Cornwall (2015) quotes several experts on the efficacy of the Deepwater Horizon subsea injection and further use of the technique. Eygun et al. (2014) and Michel et al. (2014a,b) note the incorporation of subsea equipment into contingency plans and exercises.

Lewis et al. (2014), Munro et al. (2015) and Mullin (2016) review other options for sub-sea well control and note the placement of equipment to carry this out.

Powell and Chauhan (2016) measure dynamic interfacial tension and dilational rheology, which have not been previously reported for the Corexit 9500 system. Measurements show that increasing the aqueous salinity to approximately that of sea water drastically increases Corexit

9500s adsorption rates and lowers interfacial tensions. Specifically, the interfacial tension decreases from a pure interface value of 22.4 mN/m to approximately 2 mN/m at 10 wt% Corexit 9500 and 0.01 wt% Corexit 9500 for the fresh and salt water systems, respectively. The time for achieving equilibrium is inversely proportional to the concentration. Dynamic and equilibrium interfacial tensions for both systems are well described by a simplified predictive model for several orders of magnitude in concentration. Finally, moderately high dilational moduli values which are frequency independent and primarily elastic in nature were measured. The time scales for adsorption reported here could be useful in designing the process for spraying the dispersant in deep-sea applications. The model parameters, although not physically correct due to the assumption of a single component system, could be useful in predicting the adsorption of the sprayed dispersant to the rising oil plume. The parameters measure indicate that Corexit 9500 would be very soluble in seawater. Since the oil portion of the data was not measured, the partitioning into oil is not known.

Results from Previous Literature Reviews

2014 The Deepwater Horizon spill was marked by extensive sub-surface use of oil spill dispersants. 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. 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, 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

Introduction

Dioctyl sulfosuccinate (DOSS) is a major component of the Corexit dispersants and has an aquatic toxicity of approximately double that of the whole dispersant. DOSS is found in both waters nearby and distant from areas where dispersant was used. The other dispersant components have also been monitored with generally lesser sensitivity.

There were no new studies during this time period, however useful results were generated in other studies.

Results from Previous Literature Reviews

2014

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.

4.8 Separation of Dispersants from Oil Droplets

Introduction

It is well known that dispersant components separate from oil droplets once a dispersion is formed. There are some classical studies on this in the colloid literature, but few in the oil spill literature.

Summary and Conclusions

Little progress was made in the past 3 years in terms of understanding the separation of dispersant components from oil droplets.

Detailed Study Summaries

Kirby et al. (2015) study two surfactants, Aerosol-OT (AOT) and Tween 80 which are two of the main surfactants in commercial dispersants used in response to oil spills. Understanding how multicomponent surfactant systems interact at oil/aqueous interfaces is crucial for improving both dispersant design and application efficacy. This is true of many multicomponent formulations; a lack of understanding of competition for the oil/water interface hinders formulation optimization. In this study, they characterized the sequential adsorption behavior of AOT on squalane/aqueous interfaces that have been precoated with Tween 80. A microtensiometer was used to measure the dynamic interfacial tension of the system. Tween 80 either partially or completely irreversibly adsorbs to squalane/aqueous interfaces when rinsed with deionized water. These Tween 80 coated interfaces are then exposed to AOT. AOT adsorption increases with AOT concentration for all Tween 80 coverages, and the resulting steady-state interfacial tension values are interpreted using a Langmuir isotherm model. In the presence of 0.5 M NaCl, AOT adsorption significantly increases due to counterion charge screening of the negatively charged head groups. The presence of Tween 80 on the interface inhibits AOT adsorption, reducing the maximum surface coverage as compared to a clean interface. Tween 80 persists on the interface even after exposure to high concentrations of AOT.

Results from Previous Literature Reviews
2008

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.

2014

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.

4.9 Human Health Aspects

Introduction

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.

Summary and Conclusions

Several studies of different types were applied. Many of the results could be considered preliminary since they were one-off studies and many indicated marginal results.

Application of several standard procedures indicated that:

- The health risk to children from touching beach sand that had been contaminated by oil and/or dispersant was low.
- The health risk from approved sea food was low and maybe less than the risk from inland sea food.
- There was low risk to cleanup workers of exposure to inhalation of high levels of toxicants however blood levels of some products were found.
- There was lung epithelial toxicity by Corexit dispersants.
- Corexit was found to be somewhat cytotoxic.
- It was found that there were stress symptoms such as depression and anxiety amount cleanup works as well as their families.
- DOSS, an ingredient of Corexit, was found to be an obesogen, however one would need to ingest DOSS.

Detailed Study Summaries

Black et al. (2016) evaluated the health risk to children who potentially contacted beach sands impacted by oil spill chemicals and chemicals in the oil, from the Deepwater Horizon disaster. To identify chemicals of concern, the U.S. Environmental Protection Agency's (EPA's) monitoring data collected during and immediately after the spill were evaluated. This dataset was supplemented with measurements from beach sands and tar balls collected five years after the spill. Of interest is that metals in the sediments were observed at similar levels between the two sampling periods; some differences were observed for metals levels in tar balls. Although PAHs were not observed five years later, there is evidence of weathered-oil oxidative by-products. Comparing chemical concentration data to baseline soil risk levels, three metals (As, Ba, and V) and four PAHs (benzo a pyrene, benz a anthracene, benzo b fluoranthene, and dibenz a,h anthracene) were found to exceed guideline levels prompting a risk assessment. For acute or sub-chronic exposures, hazard quotients, computed by estimating average expected contact behavior, showed no adverse potential health effects. For cancer, computations using 95% upper confidence limits for contaminant concentrations showed extremely low increased risk in the 10^{-6} range for oral and dermal exposure from arsenic in sediments and from dermal exposure from benzo a pyrene and benz a anthracene in weathered oil. Overall, results suggest that health risks are extremely low, given the limitations of available data. Limitations of this study are associated with the lack of toxicological data for dispersants and oil-spill degradation products. They also recommend studies to collect quantitative information about children's beach play habits, which are necessary to more accurately assess exposure scenarios and health risks.

Bowers et al. (2016) studied the Corexit-enhanced Water Accommodated Fraction (CWAF) of DWH crude oil which contains PPARγ transactivation activity, which is attributed to dioctyl sodium sulfosuccinate (DOSS), a probable obesogen. In addition to its use in oil dispersants, DOSS is commonly used as a stool softener and food additive. Because PPARγ functions as a heterodimer with RXRα to transcriptionally regulate adipogenesis, they investigated the potential of CWAF to transactivate RXRα and herein demonstrated that the Corexit component Span 80 has RXRα transactivation activity. Span 80 bound to RXRα in the low micromolar range and promoted adipocyte differentiation of 3T3-L1 preadipocytes. Further, the combination of DOSS and Span 80 increased 3T3-L1 adipocyte differentiation substantially more than treatment with either chemical individually, likely increasing the obesogenic potential of Corexit dispersants. From a public health standpoint, the use of DOSS and Span 80 as food additives heightens concerns regarding their use and mandates further investigations.

Chen and Reese (2016) study Retinol (vitamin A) signaling, mediated by all-trans retinoic acid (RA), which is essential for neural tube formation and the development of many organs in the embryo. The physiological levels of RA in cells and tissues are maintained by the retinol signaling pathway (RSP), which controls the biosynthesis of RA from dietary retinol and the catabolism of RA to polar metabolites for removal. RA is a potent activating ligand for the RAR/RXR nuclear receptors. Through RA and the receptors, the RSP modulates the expression of many developmental genes; interference with the RSP is potentially teratogenic. In this study, the mouse P19 embryonal pluripotent cell, which contains a functional RSP, was used to evaluate the effects of the Corexit dispersants on retinol signaling and associated neuronal differentiation. The results showed that Corexit-EC9500A was more cytotoxic than Corexit-EC9527A to P19 cells. At non-cytotoxic doses, Corexit-EC9527A inhibited retinol-induced expression of the Hoxa1 gene, which encodes a transcription factor for the regulation of body patterning in the embryo. Such inhibition was seen in the retinol- and retinal- induced, but not RA-induced, Hoxa1 up-regulation, indicating that the Corexit chemicals primarily inhibit RA biosynthesis from retinal. In addition, Corexit-EC9527A suppressed retinol-induced P19 cell differentiation into neuronal cells, indicating potential neurotoxic effect of the chemicals under the tested conditions. The surfactant ingredient, dioctyl sodium sulfosuccinate (DOSS), may be a major contributor to the observed effect of Corexit-EC9527A in the cell.

Green et al. (2014) carried out a 5-yr study to identify potential long-term health effects to workers involved in the response to the Deepwater Horizon Oil spill. The levels of contaminant exposure received by Deepwater Horizon response workers were evaluated and the aspects of exposure were compared to the limited amount of information available for the Prestige oil spill response for which researchers have reported evidence of long-term health effects. Monitored chemicals included: various measures of oil and its constituents (e.g., petroleum distillates, BTEX compounds, and H_2S), the dispersants employed (e.g., 2-butoxyethanol), and combustion by-products (e.g., PAH). The frequencies and concentrations of chemicals detected in air were reviewed; and using benzene as an example, evaluated to determine whether exposures led to adverse acute and chronic effects on human health. Approximately 89% of the measurements for Deepwater Horizon cleanup workers were less than measurements reported for paid cleanup workers during the Prestige spill, largely the result of the differing nature of the two releases.

Liu et al. (2016) evaluated the transcriptomic profile of human airway epithelial cells grown under treatment of crude oil, the dispersants Corexit 9500 and Corexit 9527, and oil-dispersant mixtures. They identified a very strong effect of Corexit 9500 treatment, with 84 genes (response genes) differentially expressed in treatment vs. control samples. They found an interactive effect of oil-dispersant mixtures; while no response gene was found for Corexit 9527 treatment alone, cells treated with Corexit 9527 + oil mixture showed an increased number of response genes (46 response genes), suggesting a synergic effect of 9527 with oil on airway epithelial cells. Through GO (gene ontology) functional term and pathway-based analysis, they identified upregulation of gene sets involved in angiogenesis and immune responses and downregulation of gene sets involved in cell junctions and steroid synthesis as the prevailing transcriptomic signatures in the cells treated with Corexit 9500, oil, or Corexit 9500 + oil mixture. Interestingly, these key molecular signatures coincide with important pathological features observed in common lung diseases, such as asthma, cystic fibrosis and chronic obstructive pulmonary disease. The study provides mechanistic insights into the detrimental effects of oil and oil dispersants to the respiratory system and suggests significant health impacts of the recent BP oil spill to those involved in the cleaning operation.

Liu et al. (2017) performed RNA-seq analyses of a system of human airway epithelial cells treated with the BP crude oil and/or dispersants Corexit 9500 and Corexit 9527 that were used to help break up the oil spill. Based on the RNA-seq data, they then systemically analyzed the transcriptomic perturbations of the cells at the KEGG pathway level using two pathway-based analysis tools, GAGE (generally applicable gene set enrichment) and GSNCA (Gene Sets Net Correlations Analysis). The results suggested a pattern of change towards carcinogenesis for the treated cells marked by upregulation of ribosomal biosynthesis (hsa03008) ($p = 1.97E^{-13}$), protein processing (hsa04141) ($p = 4.09E^{-7}$), Wnt signaling (hsa04310) ($p = 6.76E^{-3}$), neurotrophin signaling (hsa04722) ($p = 7.73E^{-3}$) and insulin signaling (hsa04910) ($p = 1.16E^{-2}$) pathways under the dispersant Corexit 9527 treatment, as identified by GAGE analysis. Furthermore, through GSNCA analysis, they identified gene co-expression changes for several KEGG cancer pathways, including small cell lung cancer pathway (hsa05222, $p = 9.99E^{-5}$), under various treatments of oil/dispersant, especially the mixture of oil and Corexit 9527. Overall, the results suggested carcinogenic effects of dispersants (in particular Corexit 9527) and their mixtures with the BP crude oil, and provided further support for more stringent safety precautions and regulations for operations involving long-term respiratory exposure to oil and dispersants.

Murphy et al. (2016) examined approximately 10% of oil spill literature (1255 of over 11,000 publications) published from 1968 to 2015. They find that, despite its episodic nature, oil spill research is a rapidly expanding field with a growth rate faster than that of science as a whole. There is a massive post-Deepwater Horizon shift of research attention to the Gulf of Mexico, from 2% of studies in 2004–2008 to 61% in 2014–2015, thus ranking Deepwater Horizon as the most studied oil spill. There is, however, a longstanding gap in research in that only 1% of studies deal with the effects of oil spills on human health.

Resnik et al. (2015) explore ethical issues that arose in the Gulf Long-term Follow-up Study (GuLF STUDY) and cleanup workers. Ethical issues encountered by GuLF STUDY investigators included a) minimizing risks and promoting benefits to participants, b) obtaining valid informed consent, c) providing financial compensation to participants, d) working with vulnerable participants, e) protecting participant confidentiality, f) addressing conflicts of interest, g) dealing with legal implications of research, and h) obtaining expeditious review from the institutional review board (IRB), community groups, and other committees. To ensure that ethical issues are handled properly, it is important for investigators to work closely with all agencies during the development and implementation of research and to consult with groups representing the community. Researchers should consider developing protocols, consent forms, survey instruments, and other documents prior to the advent of a public health emergency to allow for adequate and timely review by constituents. When an emergency arises, these materials can be quickly modified to take into account unique circumstances and implementation details.

Rung et al. (2015) conducted a survey of wives of cleanup workers of the Deepwater Horizon. The prevalence of depression in the sample was 31%, 33% reported increases in domestic fights, 31%–32% reported memory loss post-spill, and 39%–43% reported an inability to concentrate post-spill. An index representing total exposure to the spill, including both direct physical exposure to the oil/dispersants as well as indirect economic impact from the consequences of the oil spill, was constructed from 12 questionnaire items (mean 4.2, out of a possible range of 0–12) and further subdivided into physical exposure (mean score 1.6, out of a possible range of 0–6) and economic exposure indices (mean score 2.4, out of a possible range of 0–6). These results suggest that exposure to the Deepwater Horizon Oil Spill was associated with depression, increase in domestic partner fights, memory loss, and an inability to concentrate among female partners of oil spill clean-up workers.

Sammarco et al. (2016) review hydrocarbons in humans as a result of the DWH spill. During/after the BP/Deepwater Horizon oil spill, cleanup workers, fisherpersons, SCUBA divers, and coastal residents were exposed to crude oil and dispersants. These people experienced acute physiological and behavioral symptoms and consulted a physician. They were diagnosed with petroleum hydrocarbon poisoning and had blood analyses analyzed for volatile organic compounds; samples were drawn 5–19 months after the spill had been capped. The researchers examined the petroleum hydrocarbon concentrations in the blood. The aromatic compounds m,p-xylene, toluene, ethylbenzene, benzene, o-xylene, and styrene, and the alkanes hexane, 3-methylpentane, 2-methylpentane, and iso-octane were detected. Concentrations of the first four aromatics were not significantly different from US National Health and Nutritional Examination Survey/US National Institute of Standards and Technology 95th percentiles, indicating high concentrations of contaminants. The other two aromatics and the alkanes yielded equivocal results or significantly low concentrations. The data suggest that single-ring aromatic compounds are more persistent in the blood than alkanes and may be responsible for the observed symptoms. People should avoid exposure to crude oil through avoidance of the affected region, or utilizing hazardous materials suits if involved in cleanup, or wearing hazardous waste operations and emergency response suits if SCUBA diving. Concentrations of alkanes and PAHs in the blood of coastal residents and workers should be monitored through time well after the spill has been controlled.

Sathiakumar et al. (2017) characterized risk pertaining to seafood consumption patterns following the Deepwater Horizon oil spill, among school children (K to 4th grade) residing in close proximity to the Gulf of Mexico in Mobile County, Alabama. Responses on seafood consumption pattern including the type of seafood and intake rate during the pre- and post oil spill periods, from parents of 55 school children from three schools located <20 mile radius from the Gulf of Mexico shoreline (coastal group) were compared with those from parents of 55 children from three schools located ≥20 miles away from the shoreline (inland group). They also estimated levels of concern (LOCs) in seafood for selected chemicals found in crude oil including heavy metals, and polycyclic aromatic hydrocarbons (PAH), and dioctyl sodium sulfosuccinate (DOSS), the primary compound in dispersants. The coastal group ate more seafood consisting primarily of crustaceans (62% vs. 42%) and fin fish (78% vs. 58%) from the Gulf of Mexico compared to the inland group, while the inland group ate more fin fish not found in the Gulf of Mexico (62% vs. 33%). In the post-oil spill time period, both groups substantially reduced their consumption of sea food. On average, the coastal group ate ≥2 seafood meals per week, while the inland group ate ≤1 meal per week; these frequency patterns persisted in the post oil-spill period. Comparison of the estimated LOCs with contaminant levels detected in the seafood tested by the Food and Drug Administration and National Oceanic and Atmospheric Administration, post-oil spill, found that the levels of PAHs, arsenic, and DOSS in seafood were 1–2 orders of magnitude below the LOCs calculated in their study. Levels of methyl mercury (MeHg) in the seafood tested pre- and post-oil spill were higher than the estimated LOCs suggesting presence of higher levels of MeHg in seafood independent of the oil spill. In sum, the study found higher than average seafood consumption among children along the Mobile coastal area when compared to the inland children and the National Health and Nutrition Examination Survey (NHANES) estimates. Risk characterization based on the LOCs indicated no increase in risk of exposure despite higher seafood consumption rates among the study population compared to the general population.

Singleton et al. (2016) employed portable airborne particulate matter samplers and a genetically engineered bacterial reporter system (umu-ChromoTest from EBPI) to determine levels of genotoxicity of air samples collected from highly contaminated areas of coastal Louisiana including Grand Isle, Port Fourchon, and Elmer's Island in the spring, summer and fall of 2011, 2012, 2013 and 2014. Air samples collected from a non-contaminated area, Sea Rim State Park, Texas, served as a control for background airborne genotoxic particles. In comparison to controls, air samples from the contaminated areas demonstrated highly significant increases in genotoxicity with the highest values registered during the month of July in 2011, 2013, and 2014, in all three locations. This seasonal trend was disrupted in 2012, when the highest genotoxicity values were detected in October, which correlated with hurricane Isaac landfall in late August of 2012, about five weeks before a routine collection of fall air samples. The data demonstrate: (i) high levels of air genotoxicity in the monitored areas over last four years post DWH oil spill; (ii) airborne particulate genotoxicity peaks in summers and correlates with high temperatures and high humidity; and (iii) this seasonal trend was disrupted by the hurricane Isaac landfall, which further supports the concept of a continuous negative impact of the oil spill in this region.

Starbird et al. (2015) examine how information about an oil spill, its impacts, and the use of dispersants to treat the oil, moved through social media and the surrounding Internet during the 2010 BP Deepwater Horizon oil spill. Using a collection of tweets captured during the spill, they employ a mixed-method approach including an in-depth qualitative analysis to examine the content of Twitter posts, the connections that Twitter users made with each other, and the links between Twitter content and the surrounding Internet. This article offers a range of findings to help practitioners and others understand how social media is used by a variety of different actors during a slow-moving, long-term, environmental disaster. They enumerate some of the most salient themes in the Twitter data, noting that concerns about health impacts were more likely to be communicated in tweets about dispersant use, than in the larger conversation. They describe the accounts and behaviors of highly retweeted Twitter users, noting how locals helped to shape the network and the conversation. Importantly, their results show the online crowd wanting to participate in and contribute to response efforts, a finding with implications for future oil spill response.

Temkin et al. (2016) investigated the environmental contamination resulting from the Deepwater Horizon (DWH) oil spill, including the use of the oil dispersant Corexit (a suspected obesogen) in remediation efforts, to determine whether obesogens were released into the environment during this incident. They also sought to improve the sensitivity of obesogen detection methods in order to guide post-toxicological chemical assessments. Peroxisome proliferator-activated receptor gamma (PPARγ) transactivation assays were used to identify putative obesogens. Solid-phase extraction (SPE) was used to sub-fractionate the water-accommodated fraction generated by mixing COREXIT, cell culture media, and DWH oil (CWAF). Liquid chromatography-mass spectrometry (LC-MS) was used to identify components of fractionated CWAF. PPAR response element (PPRE) activity was measured in PPRE-luciferase transgenic mice. Ligand-binding assays were used to quantitate ligand affinity. Murine 3T3-L1 preadipocytes were used to assess adipogenic induction. It was found that serum-free conditions greatly enhanced the sensitivity of PPARγ transactivation assays. CWAF and COREXIT had significant dose-dependent PPARγ transactivation activities. From SPE, the 50:50 water:ethanol volume fraction of CWAF contained this activity, and LC-MS indicated that major components of Corexit contribute to PPARγ transactivation in the CWAF. Molecular modeling predicted several components of Corexit might be PPARγ ligands. They classified dioctyl sodium sulfosuccinate (DOSS), a major component of Corexit, as a probable obesogen by PPARγ transactivation assays, PPAR-driven luciferase induction in vivo, PPARγ binding assays (affinity comparable to pioglitazone and arachidonic acid), and in vitro murine adipocyte differentiation. They concluded that DOSS is a putative obesogen worthy of further study, including epidemiological and clinical investigations into laxative prescriptions consisting of DOSS.

Results from Previous Literature Reviews

2014 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.

4.10 Effects on Photooxidation and Photodegradation

Summary and Conclusions

Limited studies have been carried out showing that dispersants enhance the photodegradation of PAHs resulting in increased toxicity of the oil and dispersant under the influence of sun.

Detailed Study Summary

Fu et al. (2017) studied the effects of 3 oil dispersants (Corexit EC9500A, Corexit EC9527A and SPC 1000) on the photodegradation of pyrene under simulated sunlight. Both Corexit dispersants enhanced the photodegradation of pyrene, while SPC1000 slightly inhibited the reaction. Span 80 and Tween 85 were the key ingredients causing the effects, though the underlying mechanisms differed. Span 80 enriches pyrene in the upper layer of water column, whereas Tween 85 induces a photosensitization process. Two reactive oxygen species, $^1O_2$ and O_2[rad]−, were found responsible for pyrene photodegradation, though the presence of EC9500A suppressed the $^1O_2$ pathway. In terms of photodegradation products, EC9500A enhanced generation of polyaromatic intermediates, such as phenaleno[1,9-cd][1,2]dioxine, 1-hydroxypyrene, and 1,8-pyrenequinone, but did not alter the classical photodegradation pathway. The Corexit dispersants were more prone to photochemical decomposition, with multiple by-products detected.

Results from Previous Literature Reviews

2008 The few tests of photo-enhanced toxicity clearly show that oil and especially dispersed oil is increased by UV light. Increases of 1.5 to 4 for noted for physically-dispersed oil and from about 4 to 48 times for chemically-dispersed oil. This photo-enhanced toxicity is particularly applicable to dispersant application in shallow waters.

4.11 Modeling

Introduction

Modeling is becoming an increasing activity and source of information as well as the traditional provision of predictions. In this review, almost every conceivable facet of oil spill and oil spill fate and behaviour is modeled. If modeling results are accurate, these data are very useful. Some of the studies have involved obtaining data, typically from laboratory model systems, to develop the modeling algorithms.

Summary and Conclusions

There are many types of models summarized in this review. The following points can be made:

- Many 3-dimentional oil spill models are published, whereas before, most were 2-dimentional. This 3-d capability enables the calculation of dispersion.
- More models now include a variety of facets including movement, impact, fate and effects.
- An important field of modeling is the understanding of processes. In this time period, there is much focus on understanding the production of droplets and their sizes and size ranges.
- Extensive effort was placed on studying the dynamics of the Deepwater Horizon spill, especially that of the sub-sea discharge.
- There are now chemical dispersion models with some basis on empirical data, albeit rather old.

- There exists a strong need for more actual data at full scale to calibrate and develop models.
- Over-reliance on models to understand natural systems can occur in the absence of actual data.

Detailed Study Summaries

Afenyo et al. (2016a,b; 2017) reviewed and developed a multimedia fate and transport model using a fugacity-based approach. Similarly, Aghajanloo and Pirooz (2016), Kuang et al. (2016) and Guo et al. (2014) developed 3-d models incorporating many behaviors plus dispersion. Likewise, Azevedo et al. (2014), Bi and Si (2014) and Brenner (2015) describe 3-d models.

Bejarano and Mearns (2015) prepared a model which compares the risk to biota based on a number of assumptions. The model could be used to compare response options.

Cai et al. (2014a) modeled the fate of individual dispersant components in the Deepwater Horizon spill.

Chow et al. study the influence of droplet size on subsea plume behavior using glass beads of relevant size to represent droplets.

Dambros et al. (2014) developed a model including dispersion. Similarly, García-Olivares et al. (2014) describe a new model to provide a basis for predicting large spills.

De Serio and Mossa (2016) used monthly surface current data in the Ionian Sea to obtain time-averaged values of the turbulent velocity components, turbulent kinetic energy and turbulent time scales. Based on these calculated turbulent parameters, the horizontal eddy diffusivity was computed with the hypothesis of homogeneous turbulence using two methods, which provided results with the same order of magnitude. These results are of interest for numerical dispersion models. Finally, only referring to the month of December 2014, the time series of the crude oil concentration was available at the station and was examined in depth. The field data enabled them to conclude that the crude oil dispersion process is influenced by the sea turbulence.

Fingas (2017b) described a new model of oil spill dispersion. A model was constructed utilizing four basic processes. Initial dispersion was calculated using the Delvigne equation adjusted to chemical dispersion, then the dispersion was distributed over the mixing depth, as predicted by the wave height. Then the droplets rise to the surface according to Stokes' law. Oil on the surface, from the rising oil and that undispersed, is re-dispersed. The droplets in the water column are subject to coalescence as governed by the Smoluchowski equation. A loss or portion of the amount dispersed, is input to account for the production of small droplets that rise slowly and are not re-integrated with the main surface slick. This is the amount taken as 'permanently' dispersed. More than 1000 runs were carried out with variations of the models. The runs show that the most important factor to the time to extinction of the surface slick, is the mixing depth of the sea as predicted from wind speed. The second most important factor is the viscosity of the starting oil. The model predicts the maximum viscosity that would be dispersed given wind and wave conditions. Variations of the model were developed to enable inputs of only wind speed and oil viscosity. A simplified prediction model was created using regression. The model outputs illustrate the time history of oil-in-water emulsions and the various influences on this time history. The long-term fate of the oil is not modeled.

Gross et al. (2014) discusses the rapid partition of hydrocarbons during the first hours after release of petroleum at sea. Limited information is available about very early evaporation and dissolution processes. The authors report on the composition of the oil slick during the first day after a permitted, unrestrained 4.3 m^3 oil release conducted on the North Sea. Rapid mass transfers of volatile and soluble hydrocarbons were observed, with >50% of ≤C17 hydrocarbons disappearing within 25 h from this oil slick of <10 km^2 area and <10 μm thickness. For oil sheens, >50% losses of ≤C16 hydrocarbons were observed after 1 h. They developed a mass transfer model to describe the evolution of oil slick chemical composition and water column hydrocarbon concentrations. The model was parametrized based on environmental conditions and hydrocarbon partitioning properties estimated from comprehensive two-dimensional gas chromatography (GC×GC) retention data. The model correctly predicted the observed fractionation of petroleum hydrocarbons in the oil slick resulting from evaporation and dissolution. This is important in that this loss occurred without the use of dispersants. If dispersants had been used this loss could have been misinterpreted as dispersion.

Jaggi et al. (2017) noted that the conventional shake flask technique for determining oil-water partition ratios of benzene, toluene, ethylbenzene and xylene (BTEX) cannot accurately assess the extremes of high pressure and low water temperatures found in submarine oil spill conditions. An oil-water partitioning device has been constructed to experimentally simulate the partition behavior of BTEX compounds under submarine oil spill conditions, using simulated live oil (methane-charged), with saline waters over a range of pressure (2–15 MPa) and temperature (4–20 °C). Within the investigated ranges, the partition ratios of BTEX compounds increase proportionally with an increase in methane charging pressure (oil saturation pressure) and the degree of BTEX alkylation, and decrease with increase in temperature. The variation of the partition ratio values due to changes in system pressure and increasing oil methane concentration, is much more significant than those seen due to change in the temperature over the range studied. This data may be used in near-field and far-field distribution modeling of the environmental fate of highly toxic BTEX compounds, derived from submarine oil spills and their impact on the ecosystem. The parameters will also aid in the prediction of oil migration and dispersion away from the spill thus helping to improve response strategies.

Johansen et al. (2015) present a new semi-empirical model for oil droplet size distributions generated by single breaking wave events. Empirical data was obtained from laboratory experiments with different crude oils at different stages of weathering. The paper begins with a review of the most commonly used model for natural dispersion, and then a presentation of the laboratory study on oil droplet size distributions formed by breaking waves conducted by SINTEF on behalf of the NOAA/UNH Coastal Response Research Center. The next section presents the theoretical and empirical foundation for the new model. The model is based on dimensional analysis and contains two non-dimensional groups; the Weber and Reynolds number. The model was validated with data from a full scale experimental oil spill conducted in the Haltenbanken area offshore Norway in July 1982.

Lambert and Variano (2016) quantify the collision of oil droplets and marine aggregates using existing collision rate equations. Results show that interaction of drops and aggregates can substantially influence the drop size distribution, but like all such processes this result is sensitive to the local concentration of oil and aggregates. The analysis also shows that as the size distribution of oil droplets shifts toward larger droplets, a greater fraction of the total oil volume collides with marine aggregates. This result is robust to a variety of different assumptions in the collision model. Results also show that there is not always a dominant collision mechanism. For example, when droplets and aggregates are both close to 10 μm in radius, shear and differential settling contribute nearly equally to the collision rate.

Lanotte et al. (2016) investigated the effect of vertical shear on the horizontal dispersion properties of passive tracer particles on the continental shelf of the South Mediterranean using observation and model data. In-situ current measurements reveal that vertical gradients of horizontal velocities in the upper mixing layer decorrelate quite fast (~1/ day), whereas an eddy-permitting ocean model, such as the Mediterranean Forecasting System, tends to overestimate such decorrelation time because of finite resolution effects. Horizontal dispersion, simulated by the Mediterranean Sea Forecasting System, is mostly affected by: (1) unresolved scale motions, and mesoscale motions that are largely smoothed out at scales close to the grid spacing; (2) poorly resolved time variability in the profiles of the horizontal velocities in the upper layer. For the case study, they have analysed, they show that a suitable use of deterministic kinematic parametrizations is helpful to implement realistic statistical features of tracer dispersion in two and three dimensions. The approach here suggested provides a functional tool to control the horizontal spreading of small organisms or substance concentrations, and is thus relevant for marine biology, pollutant dispersion as well as oil spill applications.

Li et al. (2017) developed an oil droplet size model for turbulent conditions based on non-dimensional analysis of disruptive and restorative forces, which is applicable to oil droplet formation under both surface breaking-wave and subsurface-blowout conditions, with or without dispersant application. This was accomplished using a Weber number formulation and restricting droplet size distributions. This model was calibrated and validated with droplet size data obtained from controlled laboratory studies of dispersant-treated and non-treated oil in subsea dispersant tank tests and field surveys.

Li et al. (2014, 2016a) model response options noting that speed of response is more important than most other factors.

Li et al. (2016b) tested the applicability of modified Weber number scaling with Alaska North Slope (ANS) crude oil, and developing a Reynolds number scaling approach for oil droplet size prediction for high viscosity oils. Dispersant-to-oil-ratio and empirical coefficients were also quantified. Finally, a two-step Rosin-Rammler scheme was introduced for the determination of droplet size distribution. This new approach appeared more advantageous in avoiding the inconsistency in interfacial tension measurements, and consequently delivered concise droplet size prediction. Calculated and observed data correlated well based on Reynolds number scaling. The relation indicated that chemical dispersant played an important role in reducing the droplet size of ANS under different seasonal conditions. The proposed Reynolds number scaling and two-step Rosin-Rammler approaches provide a concise, reliable way to predict droplet size distribution.

Li et al. (2017) developed a surface oil entrainment model and droplet size model to estimate the flux of oil under surface breaking waves. Both equations are expressed in dimensionless Weber number (We) and Ohnesorge number (Oh, which explicitly accounts for the oil viscosity, density, and oil-water interfacial tension). Data from controlled lab studies, large-scale wave tank tests, and field observations have been used to calibrate the constants of the two independent equations. Predictions using the new algorithm compared well with the observed amount of oil removed from the surface and the sizes of the oil droplets entrained in the water column. Simulations with the new algorithm, implemented in a comprehensive spill model, show that entrainment rates increase more rapidly with wind speed than previously predicted based on the existing Delvigne and Sweeney's (1988) model, and a quasi-stable droplet size distribution ($d < \sim 50.\ \mu m$) is developed in the near surface water.

Liu and Sheng (2014) develop an oil spill model which is coupled to a current-wave model to simulate oil spill transport in aquatic environments where waves are present. The oil spill model incorporates physical-chemical processes of oil spill, and simulates oil slick transport by a circulation-driven Lagrangian Parcel model. Using the coupled oil spill model and the current-wave model CH3D-SWAN, a laboratory observed wave induced circulation and oil slick development are successfully simulated, while different current-wave coupling schemes generate different flow patterns and oil slick evolution. The modeling system is also shown to simulate Langmuir circulation and resulting oil slicks. Hypothetical scenarios of oil spill near Virginia coast during Hurricane Isabel and Irene are simulated using the oil spill model and the CH3D-Storm Surge Modeling System to assess the role of storm waves during oil spill. The spill area is significantly larger when storm waves are considered, implying waves significantly increase oil spill dispersion.

Long et al. (2016) constructed a hydraulic water quality model for the lower reaches of the Xiangjiang River, China, using the hydrodynamic module and convective diffusion module of MIKE21. Six pollution incident scenarios were simulated to investigate the transport process of pollutants, as affected by an upstream dam structure, the Changsha Comprehensive Control Project dam (CCCP). Analysis of the results suggests that the CCCP plays an essential role in controlling the transport and transformation of pollutants. With the CCCP, the process of transport is weakened, and the dispersion effect is strengthened. In particular, after the construction of the CCCP, the same amount of upstream discharge leads to lower peak pollutant concentrations and longer pollutant arrival times to each waterworks' intake, thereby alleviating the impact of water pollution incidents.

Marcotte et al., (2016) describe a Canadian oil spill modeling suite including dispersion.

Moreira et al. (2016) study the leakage of behavior in a submerged pipeline carrying oil. They adopted a two-dimensional model based on mass conservation equations, linear momentum and the model k-ϵ standard turbulence. They used the Ansys CFX for meshing with 40,510 hexahedral elements. The results of pressure fields and volumetric fraction of oil are analyzed and discussed.

Murphy et al. (2016) investigate the effects of premixing oil with chemical dispersant at varying concentrations on the flow structure and droplet dynamics within a crude oil jet transitioning into a plume in a crossflow. The study was motivated by the need to determine the fate of subsurface oil after a well blowout. The laboratory experiments consist of flow visualizations, in situ measurements of the time evolution of droplet-size distributions using holography, and particle image velocimetry to characterize dominant flow features. Increasing the dispersant concentration dramatically decreases the droplet sizes and increases their number, and accordingly, reduces the rise rates of droplets and the upper boundary of the plume. The flow within the plume consists primarily of a pair of counterrotating quasi-streamwise vortices (CVP) that characterize jets in crossflows. It also involves generation of vertical wake vortices that entrain small droplets under the plume. The evolution of plume boundaries is dominated by interactions of droplets with the CVP. The combined effects of vortex-induced velocity and significant quiescent rise velocity of large (∼5 mm) droplets closely agree with the rise rate of the upper boundary of the crude oil plume. Conversely, the much lower rise velocity of the smaller droplets in oil-dispersant mixtures results in plume boundaries rising at rates that are very similar to those of the CVP center. The size of droplets trapped by the CVP is predicted correctly using a trapping function, which is based on a balance of forces on a droplet located within a horizontal eddy.

Nepstad et al. (2015) used a modeling approach to estimate potential ingestion amounts by copepod filtration of oil droplets. The new model was implemented in the OSCAR (Oil Spill Contingency and Response) software suite, and tested for a series of oil spill scenarios and key parameters. Among these, the size of the filtered droplets was found to be the most important factor influencing the model results. Given the assumptions and simplifications of the model, filtration of dispersed crude oil by C. finmarchicus was predicted to affect the fate of 1-40% of the total released oil mass, depending on the release scenario and parameter values used, with the lower end of that range being more probable in an actual spill situation.

Niu et al. (2016) describe a modelling effort to understand the probable distribution of petroleum hydrocarbons in Port Saint John following a hypothetical release of crude oil to which dispersant is applied during different seasons. A three-dimensional model was used to simulate the transport of oil with a release of 1,000 m^3 of Arabian light crude in the summer and winter. A stochastic approach took into account the uncertainties of environmental inputs. The results were a significant reduction of oil ashore, and enhanced biodegradation with dispersant application. However, these effects were accompanied by an increase of oil in the sediment and water column, which is a concern.

North et al. (2015) evaluated the influence of initial droplet size and rates of biodegradation on the subsurface transport of oil droplets, specifically those from the Deepwater Horizon oil spill. A three-dimensional coupled-model was employed with components that included analytical multiphase plume, hydrodynamic and Lagrangian models. Oil droplet biodegradation was simulated based on first order decay rates of alkanes. The initial diameter of droplets (10-300 μm) spanned a range of sizes expected from dispersant-treated oil. Results indicate that model predictions are sensitive to biodegradation processes, with depth distributions deepening by hundreds of meters, horizontal distributions decreasing by hundreds to thousands of kilometers, and mass decreasing by 92-99% when biodegradation is applied compared to simulations without biodegradation. In addition, there are two- to four-fold changes in the area of the seafloor contacted by oil droplets among scenarios with different biodegradation rates. The spatial distributions of hydrocarbons predicted by the model with biodegradation are similar to those observed in the sediment and water column, although the model predicts hydrocarbons to the northeast and east of the well where no observations were made.

Oliveira et al. (2017) describe the physical and mathematical formulation of a three-dimensional oil dispersion model that calculates the trajectory from the seafloor to the sea surface, its assumptions and constraints. Oil dispersion is calculated through two computational routines.

The first calculates the vertical dispersion along the water column and resamples the droplets when the oil reaches the surface. The second calculates the surface displacement of the spill.

Omar et al. (2014) used a predictive mathematical oil spill model to simulate the worst oil spill case scenarios in front of the loading and discharge terminal at Jeddah Islamic Port at the Kingdom of Saudi Arabia using different oil types (Arabian heavy and Arabian light crude oil). The model fed with worst meteorological conditions data of year 2010. The study presented the trajectory of the spilled oil slick and its fate (total area of slick, volume of slick, emulsion water content, rate of evaporation and rate of natural dispersion). Conclusion and recommendations related to the oil spill risks, preparedness and response issues were studied based on the model outputs

Otero-Diaz et al. 2014 simulated droplet trajectories using the 3-D model at a Caribbean oil platform blowout which showed that droplets with a diameter of 50 μm formed a distinct subsurface plume, which was transported horizontally and could remain below the surface. This plume could have a very restricted area of impact because the dispersion is only controlled by the ocean currents which, at 1000 m depth, have a low intensity and are quite turbulent. In this case, the formed plume stayed trapped at 1000 m depth, not posing a risk to the Caribbean Coast. In contrast, droplets with diameters of 250 μm, 1 and 10 mm rose rapidly to the surface, even with different velocities (6, 10, 20 ms^{-1}).

Özgökmen et al. (2016) summarizes observations of hydrocarbon dispersion collected at the surface and at depth and the current understanding of the factors that affect the dispersion, as well as the improved ability to model and predict oil and gas transport. As a direct result of studying the area where oil and gas spread during the DWH oil spill, the forecasting capabilities have been greatly enhanced. State-of-the-art oil spill models now include the ability to simulate the rise of a buoyant plume of oil from sources at the seabed to the surface. A number of efforts have focused on improving the understanding of the influences of the near-surface oceanic layer and the atmospheric boundary layer on oil spill dispersion, including the effects of waves. In the future, oil spill modeling routines will likely be included in Earth system modeling environments, which will link physical models (hydrodynamic, surface wave, and atmospheric) with marine sediment and biogeochemical components.

Parra-Guevara and Skiba (2014) model biodegradation as two variational problems, along with the corresponding linear and quadratic programming problems, with the aim to determine optimal discharge point and optimal discharge rate of a nutrient to be released to a marine environment polluted with oil. The objective is to minimize the total discharge of nutrient into the system provided that their concentrations still reach critical values sufficient to eliminate oil residuals in affected zones through bioremediation. A tridimensional problem for the advection-diffusion equation and its corresponding model are used to simulate, estimate and control the dispersion of nutrient in a limited region. The ability of both methods is demonstrated by numerical experiments on the remediation in an oil-polluted channel by using three control zones. In particular, the experiments with the linear programming problem show that the optimal discharge rate can always be obtained with a simple combination of step functions.

Parsa et al. (2016a) investigated the vertical oil dispersion of surface oil spills in a regular wave field in a wave tank. Various waves characteristics and different volumes of oil spills are tested to assess the oil concentration variations at two sampling stations. It is found that the oil concentration due to vertical oil dispersion follows an ascending diagram to reach a maximum and then decreases while oil slick passes the location. The maximum mid-depth oil concentration at the farther sampling station was 30–50 % less than the concentration at the closer sampling station to the spill location. A 50 % increase in oil spill volume causes 30–60 % growth in oil concentrations. The relations between oil concentration and important parameters such as wave characteristics, amount of spilled oil and the distance of sampling stations from the spill location are indicated and also oil concentration variations are quantified. Two equations are derived through statistical analysis of the experimental data, which estimate the magnitude and time of maximum oil concentration.

Parsa et al. (2016b) investigated vertical oil dispersion of surface oil spills under non-breaking regular waves in a wave tank. The variation in oil concentration caused by oil dispersion in a water column was studied to determine the vertical oil dispersion profile. The experiments were performed using different waves characteristics for different volumes of oil spill to evaluate the variation in oil concentration at three depths at two sampling stations. The correlations between oil concentration and the main parameters of wave characteristics, oil spill volume, sampling depth, and distance of sampling stations to spill location were assessed. The results revealed that the trend of variation in oil concentration versus wave steepness is linear. The results obtained from experimental measurements indicated that the oil concentrations at mid-depth were 44–77 % and the concentrations near the flume bed were 12–33 % of the concentration near the water surface.

Perhar and Arhonditsis (2014) reviewed crude oil spills in aquatic environments. They note toxic effects cascade across trophic levels, affecting phytoplankton, zooplankton, fish, aquatic birds, mammals, and benthic organisms. The literature shows much work has been done detailing the toxicity of crude oil at each of the aforementioned trophic levels, but very little of this knowledge has been incorporated into modelling studies. Instead, the majority of contemporary models focus on the abiotic fate of spilled crude oil, driven by factors such as evaporation, dissolution, dispersion, sinking, and sedimentation. In this study, they present a thorough review of the role of crude oil toxicity on aquatic organisms from a food web point of view, followed by an overview of the modelling literature, and finally outline a modelling plan in which they aim to fill the biological/ecological gap in contemporary oil spill models.

Poje et al. (2014) used surface drifters providing high-frequency position data by the near-simultaneous release of hundreds of accurately tracked. They studied the structure of submesoscale surface velocity fluctuations in the Northern Gulf of Mexico. Observed two-point statistics confirm the accuracy of classic turbulence scaling laws at 200-m to 50-km scales and clearly indicate that dispersion at the submesoscales is local, driven predominantly by energetic submesoscale fluctuations. The results demonstrate the feasibility and utility of deploying large clusters of drifting instruments to provide synoptic observations of spatial variability of the ocean surface velocity field.

Rao et al. (2016) present a numerical model for predicting the droplet size distribution resulting from the interaction of turbulent oil jets with the surrounding quiescent environment. They achieve this objective by integrating traditional multiphase CFD models with a population balance approach. The developed model has been validated against the experimental observations reported by Johansen et al. 2013. The ‘mixture model’ has been employed for evaluating flow fields in the system. They restrict the study to the atomization regime, where the droplet disintegration process has a greater significance over the competing coalescence mechanism. The population balance equation has been solved using the ‘Class method’ and the disintegration of droplets has been modelled by including the breakage kernel suggested by Lehr, 2002 The developed model has been used to analyze the effect of dispersed oil phase flow rates, the presence of dispersants, and the presence of air in the jet phase on the overall size distribution of oil droplets. They also present a case which compares the droplet size distributions obtained by using the flow field evaluated by a more rigorous Eulerian Two-Fluid model over Mixture model.

Ratchagar and Hemalatha (2014) developed a model to study the physical dispersion and distribution of oil particle concentration in the presence of Coriolis force of oil spilled under solid ice cover. The movement of oil slick is obtained by employing perturbation technique and the dispersion of oil is studied using generalized dispersion model proposed by Gill (1967). The mean concentration is computed by introducing a slug of finite length separated from pure solvent using suitable impermeable barriers by varying the dimensionless time, axial distance and length of solute slug.

Restrepo et al. (2014) describe and model why wind- and current-driven flotsam, oil spills, pollutants, and nutrients, approaching the nearshore frequently appear to slow down/park just beyond the break zone, where waves break. Moreover, the portion of these tracers that beach will do so only after a long time. Explaining why these tracers park and at what rate they reach the shore has important implications on a variety of different nearshore environmental issues, including the determination of what subscale processes are essential in computer models for the simulation of pollutant transport in the nearshore. Using a simple model, they provide an explanation for the underlying mechanism responsible for the parking of tracers, not subject to inertial effects, the role played by the bottom topography, and the non-uniform dispersion which leads, in some circumstances, to the eventual landing of all or a portion of the tracers. They refer to the parking phenomenon in this environment as nearshore sticky waters.

Schwichtenberg et al. (2016) model oil in the German Bight. They note that oil dispersed in the water column remains sheltered from wind forcing, so that an altered drift path is a key consequence of using chemical dispersants. In this study, ensemble simulations were conducted based on 7 years of simulated atmospheric and marine conditions, evaluating 2,190 hypothetical spills from each of 636 cells of a regular grid covering the inner German Bight (SE North Sea). Each simulation compares two idealized setups assuming either undispersed or fully dispersed oil. Differences are summarized in a spatial map of probabilities that chemical dispersant applications would help prevent oil pollution from entering intertidal coastal areas of the Wadden Sea. High probabilities of success overlap strongly with coastal regions between 10 m and 20 m water depth, where the use of chemical dispersants for oil spill response is a particularly contentious topic. The present study prepares the ground for a more detailed net environmental benefit analysis (NEBA) accounting also for toxic effects.

Skiba and Para-Guevara (2016) describe a three-dimensional model for the dispersion of a quasi-passive substance (a pollutant or a nutrient) and its adjoint model are considered in a limited sea region. Direct and adjoint estimates are used to get dual (equivalent) estimates of the mean concentration of the substance in important zones of the region. The role of dual estimates is illustrated with a few examples. They include such oil spill problems as the search of the most dangerous point of the oil tanker route, the oil dispersion with a climatic velocity, and the dependence of the oil concentration estimates on the oil spill rate. One more example is the application of optimal bioremediation strategy for cleaning areas polluted by oil. In this case, instead of oil, the model describes the dispersion of a nutrient released to marine environment. Balanced, unconditionally stable second-order finite-difference schemes based on the splitting method for the solution of the dispersion model and its adjoint are suggested. The main and adjoint difference schemes are compatible in the sense that at every fractional step of the splitting algorithm, the one-dimensional split operators of both schemes satisfy a discrete form of Lagrange identity. In the special unforced and non-dissipative case, each scheme has two conservation laws. Every split one-dimensional problem is solved by Thomas' factorization method.

Socolofsky et al. (2015) compare oil spill model predictions for a prototype subsea blowout with and without subsea injection of chemical dispersants in deep and shallow water, for high and low gas-oil ratio, and in weak to strong crossflows. Model results are compared for initial oil droplet size distribution, the nearfield plume, and the farfield Lagrangian particle tracking stage of hydrocarbon transport. For the conditions tested (a blowout with oil flow rate of 20,000 bbl/d, about 1/3 of the Deepwater Horizon), the models predict the volume median droplet diameter at the source to range from 0.3 to 6 mm without dispersant and 0.01 to 0.8 mm with dispersant. This reduced droplet size owing to reduced interfacial tension results in a one to two order of magnitude increase in the downstream displacement of the initial oil surfacing zone and may lead to a significant fraction of the spilled oil not reaching the sea surface.

Soloviev et al. (2016) conducted laboratory experiments focused on understanding the differences between the dynamics of crude and weathered oil spills and the effect of dispersants. After deposition on the still water surface, a drop of crude oil quickly spread into a thin slick; while at the same time, a drop of machine oil did not show significant evolution. Subsequent application of dispersant to the crude oil slick resulted in a quick contraction or fragmentation of the slick into narrow wedges and tiny drops. Notably, the slick of machine oil did not show significant change in size or topology after spraying dispersant. An advanced multi-phase, volume of fluid computational fluid dynamics model, incorporating capillary forces, was able to explain some of the features observed in the laboratory experiment. As a result of the laboratory and modeling experiments, the new interpretation of the effect of dispersant on the oil dispersion process including capillary effects has been proposed, which is expected to lead to improved oil spill models and response strategies.

Spaulding et al. (2016) developed a methodology that allows estimates to be made of the upper bound for dispersion coefficients used in a spill model to ensure that barriers to spill transport are identified and accurately accounted for in the spill model. The relative dispersion of uniformly seeded Lagrangian trajectories is computed for increasing values of the dispersion coefficient until the mixing barrier is no longer effective. The dispersion coefficient, at which the mixing barrier disappears, provides a dynamical estimate of the upper bound of its value. The method has been tested using a simulation of the circulation for a few-day period during the Deepwater Horizon spill period using results from the SABGOM hydrodynamic model hindcast of surface and subsurface currents.

Svalova et al. (2015) model oil droplet size growth as a stochastic process. Geometric Brownian motion (GBM) and its stochastic differential equations are used. Bayesian inference is introduced as a tool aiding in conditions of poor sample quality. The obtained model could predict emulsion separation indicated by a sufficiently large mean and standard deviation of the droplet growth process. It could be used for emulsions of different chemical compositions, including with added dispersants, allowing to characterize their impact on the WOE stability over time.

Tarr et al. (2016) review oil weathering noting that crude oil is a complex mixture of many thousands of mostly hydrocarbon and nitrogen-, sulfur-, and oxygen-containing compounds with molecular weights ranging from below 70 Da to well over 2,000 Da. When this complex mixture enters the environment from spills, ruptures, blowouts, or seeps, it undergoes a continuous series of compositional changes that result from a process known as weathering. Spills of petroleum involving human activity generally result in more rapid input of crude oil or refined products (diesel, gasoline, heavy fuel oil, and diluted bitumens) to the marine system than do natural processes and urban runoffs. The primary physicochemical processes involved in weathering include evaporation, dissolution, emulsification, dispersion, sedimentation/flocculation, microbial degradation, and photooxidation.

Vikebø et al. (2015) used model simulations of a blow out of 4500 m^3 of crude oil per day (Statfjord light crude) for 30 days at three locations along the Norwegian coast. Eggs were modeled as released from nine different known spawning grounds, in the period from March 1st until the end of April, and all spawning products were followed for 90 days from the spill start at April first independent of time for spawning. They have modeled overlap between spawning products and oil concentrations giving a total polycyclic hydrocarbon (TPAH) concentration of more than 1.0 or 0.1 ppb (µg/l). At these orders of magnitude, they expect acute mortality or sublethal effects, respectively. In general, adding dispersants results in higher concentrations of TPAHs in a reduced volume of water compared to not adding dispersants. Also, the TPAHs are displaced deeper in the water column. Model simulations of the spill scenarios showed that addition of chemical dispersant in general moderately decreased the fraction of eggs and larvae that were exposed above the selected threshold values.

Wang and Adams (2016) carried out an experimental study of particle plumes in ambient stratification and a mild current. In an inverted framework, the results describe the fate of oil droplets released from a deep ocean blowout. A continuous stream of dense glass beads was released from a carriage towed in a salt-stratified tank. Non-dimensional particle slip velocity (UN) ranged from 0.1 to 1.9, and particles with UN $\leq$ 0.5 were observed to enter the intrusion layer. The spatial distributions of beads, collected on a bottom sled towed with the source, present a Gaussian distribution in the transverse direction and a skewed distribution in the along-current direction. Dimensions of the distributions increase with decreasing UN. The spreading relations can be used as input to far-field models describing subsequent transport of particles or, in an inverted framework, oil droplets. The average particle settling velocity, Uave, was found to exceed the individual particle slip velocity, Us, which is attributed to the initial plume velocity near the point of release. Additionally, smaller particles exhibit a "group" or "secondary plume" effect as they exit the intrusion as a swarm. The secondary effect becomes more prominent as UN decreases, and might help explain observations from the 2000 Deep Spill field experiment where oil was found to surface more rapidly than predicted based on Us. An analytical model predicting the particle deposition patterns was validated against experimental measurements, and used to estimate near-field oil transport under the Deepwater Horizon spill conditions, with/without chemical dispersants.

Yang et al. (2015) note that once oil plumes such as those originating from underwater blowouts reach the ocean mixed layer (OML), their near-surface dispersion is influenced heavily by wind and wave-generated Langmuir turbulence. In this study, the complex oil spill dispersion process is modeled using large-eddy simulation (LES). The mean plume dispersion is characterized by performing statistical analysis of the resulting fields from the LES data. Although the instantaneous oil concentration exhibits high intermittency with complex spatial patterns such as Langmuir-induced striations, it is found that the time-averaged oil distribution can still be described quite well by smooth Gaussian-type plumes. LES results show that the competition between droplet rise velocity and vertical turbulent diffusion due to Langmuir turbulence is crucial in determining both the dilution rate and overall direction of transport of oil plumes in the OML. The smoothness of the mean plume makes it feasible to aim at modeling the oil dispersion using Reynolds-averaged type formulations, such as the K-profile parameterization (KPP) with sufficient vertical resolution to capture vertical profiles in the OML. Using LES data, they evaluate the eddy viscosity and eddy diffusivity following the KPP framework. They assess the performance of previous KPP models for pure shear turbulence and Langmuir turbulence by comparing them with the LES data. Based on the assessment a modified KPP model is proposed, which shows improved overall agreement with the LES results for both the eddy viscosity and the eddy diffusivity of the oil dispersion under a variety of flow conditions and droplet sizes.

Wu et al. (2017) examined the influence of rain-induced turbulence on oil droplet size and dispersion of oil spills in Douglas Channel in British Columbia, using historic atmospheric data. The approach was to use a model largely based on Delvigne's natural dispersion equation. Three types of oils: a light oil (Cold Lake Diluent - CLD), and two heavy oils (Cold Lake Blend - CLB and Access Western Blend - AWB) were tested. They found that the turbulent energy dissipation rate produced by rainfalls is comparable to what is produced by wind-induced waves. With the use of chemical dispersants, the results indicate that a heavy rainfall can produce the maximum droplet size of 300 μm for light oil and 1000 μm for heavy oils, and it can disperse the light oil with fraction of 22–45% and the heavy oils of 8–13%, respectively. Heavy rainfalls could be a factor for the fate of oil spills in Douglas Channel, especially for a spill of light oil and the use of chemical dispersants.

Zeinstra-Helfrich et al. (2015a) quantified the effect of oil layer thickness on entrainment and dispersion of oil into seawater, using a plunging jet with a camera system. In contrast to what is generally assumed, they revealed that for the low viscosity "surrogate MC252 oil" they used, entrainment rate is directly proportional to layer thickness. Furthermore, the volume of stably suspended small oil droplets increases with energy input (plunge height) and is mostly proportional to layer thickness. Oil pre-treated with dispersants (dispersant-oil ratio ranges from 1:50 to 1:300) is largely entrained in such large amounts of small droplets that quantification was impossible with the camera system. Very low interfacial tension causes entrainment by even minor secondary surface disturbances. Their results indicate that the effect of oil layer thickness should be included in oil entrainment and dispersion modelling.

Zeinstra-Helfrich et al. (2015b) studied how natural, chemical and mechanical dispersion could be quantified in oil spill models. For each step in the dispersion process, they review available experimental data in order to identify overall trends and propose an algorithm or calculation method. Additionally, the conditions for successful mechanical and chemical dispersion are defined. Two commonly identified key parameters in surface oil dispersion are: oil properties (viscosity and presence of dispersants) and mixing energy (often wind speed). Strikingly, these parameters play a different role in several of the dispersion sub-processes. This may explain difficulties in simply relating overall dispersion effectiveness to the individual parameters.

Zeinstra-Helfrich et al. (2016) investigated entrainment rate and initial droplet size distribution for seven different oil grades using a plunging jet apparatus with coupled camera equipment and subsequent image analysis. They found that amount of oil entrained is proportional to layer thickness and largely independent of oil properties: A dispersant dose of 1:200 did not result in a significantly different entrainment rate compared to no dispersants. Oil viscosity had a minor to no influence on entrainment rate, until a certain threshold above which entrainment was impeded. The mean droplet size scales with the modified Weber number as described by Johansen. The obtained results can help improve dispersion algorithms in oil spill fate and transport models, to aid making an informed decision about application of dispersants.

Zhao et al. (2015) considered hypothetical scenarios of releases that explore the realistic parameter space using a thoroughly calibrated DSD model, VDROP-J, and they attempted to provide bounds on the range of droplet sizes from the DWH blowout within 200 m of the wellhead. The scenarios include conditions without and with the presence of dispersants, different dispersant treatment efficiencies, live oil and dead oil properties, and varying oil flow rate, gas flow rate, and orifice diameter. The results, especially for dispersant-treated oil, are very different from recent modeling studies in the literature.

Zhao et al. (2016a) conducted a large-scale experiment of underwater oil release of 6.3 L/s through a 25.4 mm (one inch) horizontal pipe. Detailed measurements of plume trajectory, velocity, oil droplet size distribution, and oil holdup were obtained. The obtained experimental data were used for the validation of the models JETLAG and VDROP-J. Key findings include: (1) formation of two plumes, one due to momentum and subsequently plume buoyancy, and another due mostly to the buoyancy of individual oil droplets that separate upward from the first plume; (2) modeling results indicated that the traditional miscible plume models matched the momentum and buoyancy plume, but were not able to simulate the upward motion plume induced by individual oil droplets; (3) high resolution images in the jet primary breakup region showed the formation of ligaments and drops in a process known as "primary breakup". These threads re-entered the plume to re-break in a process known as "secondary breakup"; (4) the plume velocity was highly heterogeneous with regions of high velocity surrounded by stagnant regions for various durations. The results from this study revealed that the primary breakup is a key factor for quantifying the droplet size distribution which plays a crucial role in determining the ultimate fate and transport of the released oil in the marine environment. The observed spatial heterogeneity in the oil plume implies that the effectiveness of applied dispersants may vary greatly when applying directly in the discharged oil flow.

Zhu et al. (2017) carried out numerical investigation on the underwater spread and surface drift of oil spilled from a submarine pipeline under the combined action of wave and current was carried out to examine the effects of physical ocean environment, leaking flux and spilled oil density and viscosity. Reynolds-Averaged-Navier-Stokes (RANS) equations, realizable k-ε turbulence model and volume of fluid (VOF) model are employed to describe the multiphase flow, and velocity-boundary wave-making technique combined with the sponge layer damping absorber technique realizes the numerical wave flume. Oil spill experiments were conducted to validate the numerical model. The calculation results indicate that compared with the environmental conditions of still water, only current and only wave, a larger scope of underwater spreading and relatively slower rising rate and relatively faster drifting rate of oil droplets are observed under the combined action of wave and current. The leaking flux affects the floating time and dispersion concentration, while the ocean environment affects the horizontal migration and surface drifting. Under the specific conditions of present work, oil density has obvious effect on the underwater spread but limited effect on the surface drifting, while oil viscosity has little effect on both the two processes.

Zhuang et al. (2015) investigated the adsorption and desorption behaviors of dissolved petroleum hydrocarbons (DPHs) in a seawater-sediment system. Tidal flat sediment was used as the adsorbent, and crude oil was used as the adsorbate. The processes of adsorption and desorption at low concentration (<14.3 mg L-1) were described by the first-order kinetics model. The rate of desorption was slower than that of adsorption, and about 49% of the DPHs remained on the sediment. Therefore, the potential risk of pollution would exist for a long time. The adsorption isotherms could be better fitted to the linear isotherm model than the Freundlich and Langmuir models. The adsorption process is a physical adsorption, because ΔH was 39.0 kJ mol-1 which is less than 42.0 kJ mol-1. The change in n-alkanes in the process was more obvious than the aromatics; the weathering loss rate was 25.56%, the emulsification loss rate of the dispersant was 0.65% and the microbial degradation rate was 15.46%. The results showed the degradation processes of petroleum hydrocarbons in tidal flats.

Results from Previous Literature Reviews

This topic was not covered in previous reviews.

4.12 New Dispersants

Introduction

Every year there are many new suggestions for dispersant products published. This section will give a glimpse into some of the ideas.

Summary and Conclusions

In this review, approximately 30 ideas on new products are summarized. Most of these products are often based on natural products such as chitosan, xanthum or lecithin. Most of these products were not tested in a standard way and most were never developed further than a laboratory idea and a subsequent paper.

Detailed Study Summaries

Several researchers developed and tested new dispersant concepts. Riehm et al. (2017) tested Tween 80 and Lechithin as a dispersant. Pi et al. (2015, 2016) and Cai et al. (2016) use natural biopolymers, Xanthan Gum (XG), and silica nanoparticles. Abullah et al. (2016) used poly(ionic liquid)s, based on quaternized ethoxylate octadecylamine acrylamido-2-methylpropane sulfonate-co-acrylic acid (AMPS/AA) copolymer. Atta et al. (2015) developed a new dispersant based on ethoxylated octadecylammonium tosylate. Benner et al. (2015) propose a modified Chitosan. Brasileiro et al. (2015), Freitas et al. (2016), Moshtagh and Hawboldt (2015), Patra and Somasundaran (2014), and Hope and Gideon (2015) propose biosurfactants as dispersants. Ciaralli and Avezzano Comes (2016) propose a new chemical dispersant. Gong et al. (2016) modified an oil-degrading bacterium with dodecanol to produce an agent which may degrade and emulsify. Gong et al. (2015) combined bacteria with chitosan, a polysaccharide, to form a new surfactant. Laitinen et al. (2017) propose using cellulose nano-crystals as dispersants. Laorrattanasak et al. (2016) a biosurfactant developed from bacteria. Nyankson et al. (2015a, 2015b, 2016a, 2016b) propose soybean lecithin and clay nanotubes as new dispersants. Ojala et al. (2016) used cellulose nanocrystals. Owoseni et al. (2016) propose magnetic nanoparticles to release surfactants. Riehm et al. (2015 propose lecithin/Tween 80 mixtures. Rongsayamanont et al. (2017) use biosurfactants. von Klitzing et al. (2017) suggest clay nanotubes of halloysites. Wang et al. (2016) used xanthum gum. Zhang et al. (2015) report on a novel zwitterionic surfactant.

4.13 Composition of Dispersants

Introduction

While the composition of most dispersants remains proprietary, the composition of Corexit 9500 was revealed in connection with the Deepwater horizon spill. The surfactants DOSS, Tween 80 and Span 90 are used along with glycols as solvents, including Dipropylene glycol n-butyl ether. Other dispersants are known to differ significantly from these components. The importance of the composition is critical when considering monitoring such as was carried out at the DWH. Individual components, particularly DOSS could be traced for dozens of kilometers around the locations where it was used.

Summary and Conclusions

Some work continues on the important facet of identifying components of dispersants with the intention of tracking these after dispersant use.

Detailed Study Summary

Bovenkamp-Langlois and Roy (2016) used sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy to investigate the dispersants for the sulfur based components. The main sulfur containing component should be dioctyl sodium sulfosuccinate (DOSS). S K-edge XANES analysis shows that the major sulfur species in both kinds of Corexit (9500A and 9527A) is sulfonic acid which is a part of DOSS. In addition, some fraction of sulfone was detected.

4.14 Surface Application

Introduction

The traditional method of dispersant application is to the surface of an oil spill either by boat or by aircraft. These methods are mature; however, minor improvements and extensions continue to be made.

Summary and Conclusions

Aerial application is largely the current application method; whereas, ship application work has largely been sidelined. Some new application packages have been developed in recent years and others improved.

Detailed Study Summaries

Brazil et al. (2015) outline the structural design of an oil dispersant system for a Dash 8 Q300 aircraft, which can be deployed during flight. The system can be installed and ready within 6 hours of the accident, and the boom deployment fold-out will take less than two minutes.

Assessments of response indicate that dispersant application may not be fast enough to prevent damage to birds in the event of small spills (Fraser and Racine, 2016; Fingas, 2016).

Robles and Serrano (2014) describe a version of the C295 military aircraft with an Oil Spill Dispersant (OSD) system to be used as an airborne platform capable spraying oil spills. A sloshing mechanical model was developed to evaluate the impact of the dispersant sloshing on the aircraft dynamics. Effects on aircraft stability, handling qualities and Pilot Induced Oscillations sensitivity characteristics were assessed carrying out exhaustive simulations analyses prior to the maiden flight. Sloshing model validation was supported by Computational Fluid Dynamics simulations and a dedicated flight test campaign.

Results from Previous Literature Reviews

2008 There was some work on application issues. Of particular significance was the development of single-point delivery systems. There are ASTM standards now covering these. Some preliminary work was carried out on gelled dispersants.

4.15 Fate of Dispersants

Introduction

Studies of the fate of dispersants in the environment as well as how dispersants influence the fate of oil, are important aspects of the assessment of the use of dispersants. Studies are gradually being focussed on this area; whereas, this area was ignored in the past.

Summary and Conclusions

Several studies the fate of dispersants and how they influence the fate of oil, have been carried out. Findings include:

- Dioctyl sulfosuccinate (DOSS) and dipropylene glycol butyl ether (DGBE), two ingredients of Corexit 9500 may be subject to photolysis and photodegrade in near-surface waters.
- The dispersant Corexit 9500 appears to inhibit the photodegradation of PAHs.
- Span 80, a surfactant ingredient in Corexit 9500, may increase the aerosolization of oil.
- Dispersants increase the sediment uptake of PAHs.

Detailed Study Summaries

Glover et al. (2014) carried out direct and sensitized photolysis experiments for two compounds chosen as surrogates for the Corexit mixture (9500 and 9527) that were applied to surface waters during the oil spill in the Gulf of Mexico. The results showed that direct photolysis did not contribute significantly to the overall degradation (max ~30%), therefore the focus shifted to sensitized photolysis, specifically the degradation stemming from the reaction rate with hydroxyl radical ($HO^{\cdot}$). The direct photochemical degradation rates for two of the compounds, dioctyl sulfosuccinate (DOSS) and dipropylene glycol butyl ether (DGBE) were measured as $4.29\times10^{-6}s^{-1}$ and $5.95\times10^{-6}s^{-1}$, respectively; whereas the overall degradation rate in ocean water was $1.56\times10^{-5}s^{-1}$ and $2.23\times10^{-5}s^{-1}$. The formation rates and apparent quantum yields for $HO^{\cdot}$ formation were determined for six ocean water samples. The values ranged from 1.81×10^{-5} near shore to 0.061×10^{-5} for the open ocean. These degradation rates suggest the possibility for photolysis to play a role in the overall fate of Corexit if the product resides near the surface.

Gong and Zhao (2017) investigated effects of Corexit EC9500A on the oxidation of phenanthrene and pyrene (two model polycyclic aromatic hydrocarbons) in Gulf coast seawater under simulated atmospheric ozone. The degradation data followed a two-stage pseudo-first order kinetics, a slower initial reaction rate followed by a much faster rate in longer time. The ozonation rate for pyrene was faster than that for phenanthrene. The presence of 18 and 180 mg/L of the dispersant inhibited the first-order degradation rate by 32–80% for phenanthrene, and 51–85% for pyrene. In the presence of 18 mg/L of the dispersant, the pyrene degradation rate increased with increasing ozone concentration, but decreased with increasing solution pH and temperature, while remaining independent of ionic strength.

Haule and Freda (2016) examined the influence of oil droplet size of highly dispersed Petrobaltic crude on the underwater visible light flux and the inherent optical properties (IOPs) of seawater, including absorption, scattering, backscattering and attenuation coefficients. On the basis of measured data and Mie theory, they calculated the IOPs of dispersed Petrobaltic crude oil in constant concentrations, but different log-normal size distributions. They also performed a radiative transfer analysis, in order to evaluate the influence on the downwelling irradiance E_d, remote sensing reflectance R_{rs} and diffuse reflectance R, using in situ data from the Baltic Sea. They found that during dispersion, there occurs a boundary size distribution characterized by a peak diameter d_0 = 0.3 μm causing a maximum E_d increase of 40 % within 0.5-m depth, and the maximum Ed decrease of 100 % at depths below 5 m. They showed that the impact of size distribution on the “blue to green” ratios of R_{rs} and R varies from 24 % increase to 27 % decrease at the same crude oil concentration.

Zhang et al. (2016) carried out laboratory aerosolization experiments and classical molecular dynamics (MD) simulations, with the objective of investigating the individual effects of the two Corexit surfactants Span 80 (non-ionic) and dioctyl sodium sulfosuccinate (DOSS, ionic), on the aerosolization of oil spill material to the atmosphere. Their simulation results show that Span 80, DOSS, and the oil alkanes n-pentadecane (C15) and n-triacontane (C30) exhibit deep free energy minima at the air/seawater interface. C15 and C30 exhibit deeper free energy minima at the interface when Span 80 is present, as compared to the situation when DOSS or no surfactants are at the interface. These results suggest that Span 80 makes these oil hydrocarbons more likely to be adsorbed at the surface of seawater droplets and carried out to the atmosphere, relative to DOSS or to the situation where no surfactants are present. These simulation trends are in qualitative agreement with their experimental observations in a bubble-column setup, where larger amounts of oil hydrocarbons are ejected when Span 80 is mixed with oil and injected into the column, as compared to when DOSS is used. Their simulations also indicate that Span 80 has a larger thermodynamic incentive than DOSS to move from the seawater phase and into the air/seawater interface. This observation is also in qualitative agreement with their experimental measurements, which indicate that Span 80 is ejected in larger quantities than DOSS. The simulations also suggest that DOSS predominantly adopts a perpendicular orientation with respect to the air/seawater interface at a dispersant to oil ratio (DOR) of 1:20, but has a slight preference to lie parallel to the interfaces at a DOR = 1:5; in both cases, DOSS molecules have their tails wide open and stretched. In contrast, Span 80 has a slight preference to align parallel to the interfaces with a coiled conformation at both DOR values.

Zhao et al. (2015) investigated effects of a prototype oil dispersant on solubilization, sorption and desorption of three model PAHs in sediment-seawater systems. Increasing dispersant dosage linearly enhanced solubility for all PAHs. Conversely, the dispersant enhanced the sediment uptake of the PAHs, and induced significant desorption hysteresis. Such contrasting effects (ad-solubilization vs. solubilization) of dispersant were found dependent of the dispersant concentration and PAH hydrophobicity. The dual-mode models adequately simulated the sorption kinetics and isotherms, and quantified dispersant-enhanced PAH uptake. Sorption of naphthalene and 1-methylnaphthalene by sediment positively correlated with uptake of the dispersant, while sorption of pyrene dropped sharply when the dispersant exceeded its critical micelle concentration (CMC). The Deepwater conditions diminished the dispersant effects on solubilization, but enhanced uptake of the PAHs, albeit sorption of the dispersant was lowered.

5 Recommendations for Further Research

The current study shows that there are several important data gaps and also several important methodology gaps (John et al., 2016). It should be first recognized that the area of dispersant research has consistently received large portions of funding, whereas other countermeasures areas such as skimming has received very little. Perhaps, dispersant research should be slowed or diminished in the future.

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. This is not the case on some studies.
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 reviewing oil spill dispersants 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 microcosms

and then ideally to the field.
10. More detailed chemical and physical studies on the interaction of oil and dispersants.

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Appendix A

References with Abstracts

Abullah, M.M.S., Al-Lohedan, H.A., Attah, A.M., Synthesis and application of amphiphilic ionic liquid based on acrylate copolymers as demulsifier and oil spill dispersant, *Journal of Molecular Liquids*, 219, pp. 54-62, 2016

The authors prepared poly(ionic liquid)s, based on quaternized ethoxylate octadecylamine acrylamido-2-methylpropane sulfonate-co-acrylic acid (AMPS/AA) copolymers using radical polymerization. New hypothesis for demulsification of petroleum crude oil:water emulsions was elucidated from zeta potential measurements of water crude oil emulsions in the presence and absence of the prepared surfactants.

Acosta, E.J., Quraishi, S. Surfactant Technologies for Remediation of Oil Spills, Chapter in: *Oil Spill Remediation: Colloid Chemistry-Based Principles and Solutions*, Wiley Publications, pp. 317-358, 2014

This chapter is on soil washing and has only a little application to oil spills on water.

Adams, J., Sweezey, M., Hodson, P.V., Oil and oil dispersant do not cause synergistic toxicity to fish embryos, *Environmental Toxicology and Chemistry*, 33, 1, pp. 107-114, 2014

Atlantic herring (Clupea harengus) embryos were exposed to water accommodated fractions (WAFs; oil dissolved in water) and chemically enhanced water accommodated fractions (CEWAFs; oil dispersed in water with Corexit 9500A) of Medium South American (MESA) crude oil. The CEWAF was approximately 100-fold more toxic than WAF based on nominal loadings of test solutions (% v/v). In contrast, the ratio of WAF and CEWAF toxicity expressed as measured oil concentrations approximated 1.0, indicating that the higher toxicity of CEWAFs was caused by an increase in exposure to hydrocarbons with chemical dispersion. In a second experiment, the chronic toxicity of Corexit 9500A and chemically dispersed heavy fuel oil 7102 (HFO 7102) to rainbow trout (Oncorhynchus mykiss) embryos was compared to chemically-dispersed Nujol, a nontoxic mineral oil. Dispersant alone was toxic, but caused different signs of toxicity than HFO 7102. Nujol at a dispersant-to-oil ratio of 1:20 was nontoxic, suggesting that dispersant was sequestered by oil and not present at toxic concentrations. In contrast, the same nominal loadings of dispersed HFO 7102 caused concentration-dependent increases in toxicity. Both experiments suggest that chemically dispersed oil was more toxic to fish embryos than solutions created by mechanical mixing due to the increased exposure of fish to petroleum hydrocarbons and not to changes in hydrocarbon toxicity. The Nujol control discriminated between the toxicity of oil and chemical dispersant and would be a practical addition to programs of dispersant testing

Adeyemo, O.K., Kroll, K.J., Denslow, N.D., Developmental abnormalities and differential expression of genes induced in oil and dispersant exposed Menidia beryllina embryos, *Aquatic Toxicology*, 168, pp. 60-71, 2015

The researchers studied the effects of the exposure of Menidia beryllina (Inland silverside) embryos at 30-48 hours post-fertilization to the water accommodated fractions of oil (WAF, 200 ppm, v/v), dispersants (20 ppm, v/v, Corexit 9500 or 9527), and mixtures of oil and each of the dispersants to produce chemically enhanced water accommodated fractions (CEWAFs) over a 72-hour period. The polyaromatic hydrocarbon (PAH) and benzene, toluene, ethylene and xylene (BTEX) constituents of the 5X concentrated exposure solutions (control, WAF, dispersants and CEWAFs) were determined and those of the 1× exposures were derived using a dilution factor. PAH, BTEX and low molecular weight PAH constituents greater than 1 ppb were observed in WAF and the dispersants, but at much higher levels in CEWAFs. The WAF and CEWAFs post-weathering were diluted at 1:5 (200 ml WAF/CEWAF: 800 ml 25 ppt saltwater) for embryo exposures. Mortality, heartbeat, embryo normalcy, abnormality types and severities were recorded. The qPCR assay was used to quantify abundances of transcripts of target genes

for sexual differentiation and sex determination, growth regulation and stress response; and gapdh served as the housekeeping gene. Temperature was 21. °C throughout the experimental period, while mortality was low and not significantly different among treatments. Heartbeat was significantly different with the lowest heartbeats recorded in Corexit 9500 and 9527 exposed embryos compared with controls. Significantly more treated embryos were in a state of deterioration, with significantly more embryos presenting arrested tissue differentiation compared with controls. Exposure to WAF, dispersants and CEWAF induced aberrant expression of all the genes, with star, dmrt-1, ghr and hsp90 being significantly down-regulated in CEWAF and cyp19b in Corexit 9527. The cyp1a and cyp19b were significantly up-regulated in CEWAFs and WAF, respectively. The molecular endpoints were most sensitive, especially the expression of star, cyp19b, cyp1a, hsp90 and could therefore be used as early indicators of long term effects of Corexit 9500 and 9527 uses in oil spill management on M. beryllina.

Afenyo, M., Khan, F., Veitch, B., Yang, M., Dynamic fugacity model for accidental oil release during Arctic shipping, *Marine Pollution Bulletin*, 111, 02-Jan, pp. 347-353, 2016a

The authors developed a multimedia fate and transport model using a fugacity-based approach.

Afenyo, M., Veitch, B., Khan, F., A state-of-the-art review of fate and transport of oil spills in open and ice-covered water, *Ocean Engineering*, 119, pp. 233-248, 2016b

The authors review fate and transport models relevant to the Arctic including dispe4sion models.

Afenyo, M., Khan, F., Veitch, B., Yang, M., A probabilistic ecological risk model for Arctic marine oil spills, *Journal of Environmental Chemical Engineering*, 5, 2, pp. 1494-1503, 2017

Afenyo et al. (2017) describe a new model incorporating a release and dispersion model, fate and transport model, and ecotoxicological modelling. Uncertainties in the proposed model and data are addressed through a probabilistic framework implemented using a fugacity model to estimate the exposure concentration in the different media that are in contact with oil. This is the focus of this paper. The 95th percentile of Predicted Exposure Concentration is compared with the 5th percentile of the Predicted No Effect Concentration to produce a Risk Quotient profile, which indicates the level of risk posed to the Arctic marine ecosystem. The application of the proposed model is illustrated through a case study. The RQ obtained is useful for making decisions on the management of safety for Arctic marine ecosystems, such as setting operational goals to prevent accidents and for designing emergency preparedness plans. The uniqueness of this work in comparison to earlier studies is that, the methodology takes into account all the significant component models needed to address a potential oil spill in a probabilistic way and demonstrated in an Arctic setting.

Aghajanloo, K., Pirooz, M.D., Three dimensional numerical modeling of oil spill behavior in marine environment, *International Journal of Environmental Research*, 8, 3. pp. 779-788, 2014

A three-dimensional model is based on an Eulerian approach.

Alekseevna, N., Seryy, S.S., Net environmental benefit analysis in planning of elimination of oil spills, Society of Petroleum Engineers - SPE Russian Petroleum Technology Conference, 2015

This paper summarizes net environmental benefit analysis (NEBA) for the Russian context.

Alexander, F.J., King, C.K., Reichelt-Brushett, A.J., Harrison, P.L., Fuel oil and dispersant toxicity to the Antarctic sea urchin (Sterechinus neumayeri), *Environmental Toxicology and Chemistry*, Vol. 9999, No. 9999, pp. 1–9, 2016

The researchers studied larval development toxicity tests using 3 life history stages of the Antarctic sea urchin (Sterechinus neumayeri) to assess the toxicity of physically dispersed, chemically dispersed, and dispersant-only water-accommodated fractions (WAFs) of an intermediate fuel oil (IFO 180, BP) and the chemical dispersant Slickgone NS (Dasic International). Despite much lower total petroleum hydrocarbon concentrations, physically dispersed fuels contained higher proportions of low-to-intermediate weight carbon compounds and were generally at least an order of magnitude more toxic than chemically dispersed fuels. Based on concentrations that caused 50% abnormality (EC_{50}) values, the embryonic unhatched blastula life stage was the least affected by fuels and dispersants, whereas the larval 4-armed pluteus stage was the most sensitive. The results indicate that the use of a fuel dispersant did not increase the hydrocarbon toxicity of IFO 180 to the early life stages of Antarctic sea urchins, relative to physical dispersal.

Al-Jawasim, M., Yu, K., Park, J.-W., Synergistic effect of crude oil plus dispersant on bacterial community in a Louisiana salt marsh sediment, *FEMS microbiology letters*, 362, 17, p. fnv144, 2015

The authors found that a combined effect of crude oil plus dispersant (Corexit 9500A) significantly altered indigenous bacterial communities in a Louisiana salt marsh sediment after 30 days of incubation. The crude oil and/or Corexit 9500A treatments triggered shifts in bacterial communities and the shift by crude oil plus Corexit 9500A was considerably different from those by either crude oil or Corexit 9500A. However, the synergistic effect of crude oil plus Corexit 9500A was not observed after 7 days of incubation; the bacterial community was slightly shifted by Corexit 9500A and the crude oil did not trigger any bacterial community shift after 7 days of incubation. The major shift was seen after 30 days DNA sequencing data indicated that Chromobacterium species was enriched in the Corexit 9500A microcosms after 7 days of incubation, while Pseudomonas, Advenella, Acidocella and Dyella spp. were enriched after 30 days of incubation. Parvibaculum was a dominant species in the crude oil microcosms after 30 days of incubation. Rhodanobacter, Dyella and Frateuria spp. were dominant in crude oil plus Corexit 9500A microcosms after 30 days of incubation. The data show that the effect of crude oil plus Corexit 9500A on bacterial community is synergistic, and thus the dispersant effect should be considered with the spilled oil to evaluate the environmental impact.

Alloy, M., Baxter, D., Stieglitz, J., Mager, E., Hoenig, R., Benetti, D., Grosell, M., Oris, J., Roberts, A., Ultraviolet Radiation Enhances the Toxicity of Deepwater Horizon Oil to Mahi-mahi (Coryphaena hippurus) Embryos, *Environmental Science and Technology*, 50, 4, pp. 2011-2017, 2016

The authors studied photoinduced toxicity following co-exposure to ultraviolet (UV) radiation and oil on Mahi-mahi (Coryphaena hippurus) embryos, which have positively buoyant, transparent eggs. These characteristics may result in mahi-mahi embryos being at particular risk from photoinduced toxicity. The goal of this study was to determine whether exposure to ultraviolet radiation as natural sunlight enhances the toxicity of crude oil to embryonic mahi-mahi. Mahi-mahi embryos were exposed to several dilutions of water accommodated fractions (WAF) from slick oil collected during the 2010 spill and gradations of natural sunlight in a fully factorial design. Co-exposure to natural sunlight and WAF significantly reduced percent hatch in mahi-mahi embryos. Effect concentrations of PAH in WAF were within the range of surface PAH concentrations reported in the Gulf of Mexico during the Deepwater Horizon spill.

Almeda, R., Bona, S., Foster, C.R., Buskey, E.J., Dispersant Corexit 9500A and chemically dispersed crude oil decreases the growth rates of meroplanktonic barnacle nauplii (Amphibalanus improvisus) and tornaria larvae (Schizocardium sp.), *Marine Environmental Research*, 99, pp. 212-217, 2014

The researchers determined the effects of Light Louisiana Sweet crude oil, dispersant Corexit 9500A, and dispersant-treated crude oil on the survival and growth rates of nauplii of the barnacle Amphibalanus improvisus and tornaria larvae of the enteropneust Schizocardium sp. Growth rates of barnacle nauplii and tornaria larvae were significantly reduced after exposure to chemically dispersed crude oil and dispersant Corexit 9500A at concentrations commonly found in the water column after dispersant application. They also found that barnacle nauplii ingested dispersed crude oil, which may have important consequences for the biotransfer of petroleum hydrocarbons through coastal pelagic food webs after a spill. Application of chemical dispersants increases the impact of crude oil spills on meroplanktonic larvae.

Almeda, R., Harvey, T.E., Connelly, T.L., Baca, S., Buskey, E.J., Influence of UVB radiation on the lethal and sublethal toxicity of dispersed crude oil to planktonic copepod nauplii, *Chemosphere*, 152, pp. 446-458, 2016a

The researchers determined the influence of natural ultraviolet B (UVB) radiation on the lethal and sublethal toxicity of dispersed crude oil to naupliar stages of the planktonic copepods Acartia tonsa, Temora turbinata and Pseudodiaptomus pelagicus. Low concentrations of dispersed crude oil (1 μL/L) caused a significant reduction in survival, growth and swimming activity of copepod nauplii after 48 h of exposure. UVB radiation increased toxicity of dispersed crude oil by 1.3-3.8 times, depending on the experiment and measured variables. Ingestion of crude oil droplets may increase photoenhanced toxicity of crude oil to copepod nauplii by enhancing photosensitization. Photoenhanced sublethal toxicity was significantly higher when T. turbinata nauplii were exposed to dispersant-treated oil than crude oil alone, suggesting that chemical dispersion of crude oil may promote photoenhanced toxicity to marine zooplankton. The results demonstrate that acute exposure to concentrations of dispersed crude oil and dispersant (Corexit 9500) commonly found in the sea after oil spills are highly toxic to copepod nauplii and that natural levels of UVB radiation substantially increase the toxicity of crude oil to these planktonic organisms.

Almeda, R., Connelly, T.L., Buskey, E.J., How much crude oil can zooplankton ingest? Estimating the quantity of dispersed crude oil defecated by planktonic copepods, *Environmental Pollution*, 208, pp. 645-654, 2016b

The group investigated and quantified defecation rates of crude oil by 3 species of marine planktonic copepods (Temora turbinata, Acartia tonsa, and Parvocalanus crassirostris) and a natural copepod assemblage after exposure to mechanically or chemically dispersed crude oil. Between 88 and 100% of the analyzed fecal pellets from three species of copepods and a natural copepod assemblage exposed for 48 h to physically or chemically dispersed light crude oil contained crude oil droplets. Crude oil droplets inside fecal pellets were smaller (median diameter: 2.4-3.5 μm) than droplets in the physically and chemically dispersed oil emulsions (median diameter: 6.6 and 8.0 μm, respectively). This suggests that copepods can reject large crude oil droplets or that crude oil droplets are broken into smaller oil droplets before or during ingestion. Depending on the species and experimental treatments, crude oil defecation rates ranged from 5.3 to 245 ng-oil/copepod . d, which represent a mean weight-specific defecation rate of 0.026 μg-oil μg/copepod . d. Considering a dispersed crude oil concentration commonly found in the water column after oil spills (1 μL/L) and copepod abundances in high productive coastal areas, copepods may defecate ~1.3-2.6 mg-oil m^{-3} d^{-1}, which would represent ~0.15%-0.30% of the total dispersed oil per day. The results indicate that ingestion and subsequent defecation of crude oil by planktonic copepods has a small influence on the overall mass of oil spills in the short term, but may be quantitatively important in the flux of oil from surface water to sediments and in the transfer of low-solubility, toxic petroleum hydrocarbons into food webs after crude oil spills.

ASTM D3328-16, Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography, ASTM International, Conshohocken, PA, 2016

ASTM F1779-16, Standard Practice for Reporting Visual Observations of Oil on Water, ASTM International, Conshohocken, PA, 2016

ASTM F2534-17, Standard Guide for Visually Estimating Oil Spill Thickness on Water, ASTM International, Conshohocken, PA., 2017

ASTM F1209, Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Ponds and Sloughs, ASTM International, Conshohocken, PA., 2016

ASTM F1210, Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Lakes and Large Water Bodies, ASTM International, Conshohocken, PA., 2016

ASTM F1231, Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Rivers and Creeks, ASTM International, Conshohocken, PA., 2016

ASTM F1279, Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Permeable Surfaces, ASTM International, Conshohocken, PA., 2016

ASTM F1280, Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Impermeable Surfaces, ASTM International, Conshohocken, PA., 2016

ASTM F1413, Standard Guide for Oil Spill Dispersant Application Equipment: Boom and Nozzle Systems, ASTM International, Conshohocken, PA., 2016

ASTM F1460, Standard Practice for Calibrating Oil Spill Dispersant Application Equipment Boom and Nozzle Systems, ASTM International, Conshohocken, PA., 2016

ASTM F1737, Standard Guide for Use of Oil Spill Dispersant Application Equipment During Spill Response: Boom and Nozzle Systems, ASTM International, Conshohocken, PA., 2016

ASTM F1738, Standard Guide for Use of Oil Spill Dispersant Application Equipment During Spill Response: Boom and Nozzle Systems, ASTM International, Conshohocken, PA., 2016

ASTM F1872, Standard Guide for Use of Chemical Shoreline Cleaning Agents: Environmental and Operational Considerations, ASTM International, Conshohocken, PA., 2016

ASTM F2059, Standard Test Method for Laboratory Oil Spill Dispersant Effectiveness Using the Swirling Flask, ASTM International, Conshohocken, PA., 2016

ASTM F2205, Ecological Considerations for the Use of Chemical Dispersants in Oil Spill Response: Tropical Environments, ASTM International, Conshohocken, PA., 2016

ASTM F2465, Standard Guide for Oil Spill Dispersant Application Equipment: Single-point Spray Systems, ASTM International, Conshohocken, PA., 2016

ASTM F2532, Standard Guide for Determining Net Environmental Benefit of Dispersant Use, ASTM International, Conshohocken, PA., 2016

ASTM F1460, Standard Practice for Calibrating Oil Spill Dispersant Application Equipment Boom and Nozzle Systems, ASTM International, Conshohocken, PA., 2016

ASTM F3251, Standard Test Method for Laboratory Oil Spill Dispersant Effectiveness Using the Baffled Flask, ASTM International, Conshohocken, PA., 2016

ASTM F2327, Standard Guide for Selection of Airborne Remote Sensing Systems for Detection and Monitoring of Oil on Water, ASTM International, Conshohocken, PA., 2016

Atta, A.M., Al-Lohedan, H.A., Abdullah, M.M.S., ElSaeed, S.M., Application of new amphiphilic ionic liquid based on ethoxylated octadecylammonium tosylate as demulsifier and petroleum crude oil spill dispersant, *Journal of Industrial and Engineering Chemistry*, in press, 2015

The authors synthesized an amphiphilic ionic liquid by etherification of octadecylamine with tetraethylene glycol followed by quaternization with p-toluene sulfonic acid. The chemical structure was confirmed by NMR spectroscopy. The surface activity, aggregation, adsorption, and the solubility of the ethoxylated octadecylammonium tosylate were investigated. The interfacial parameters between IL aqueous solution and crude oil emulsions were determined from interfacial tension measurement. The results showed the dependence of interfacial tension on the concentration, crude oil emulsion composition and chemical structure of the prepared amphiphiles. The mechanism of aggregation and adsorption ethoxylated octadecylammonium tosylate was proposed and confirmed at different interfaces. The demulsification and oil spill dispersion efficiencies were investigated at different amphiphile concentrations. The performance of the surfactant revealed that their demulsification efficiency reached 100% and the settling time required for efficient separation decreased with increment of water contents of crude oil emulsions. Moreover, the prepared surfactant achieved oil spill dispersion efficiency more than 80% at surfactant oil ratio (1:25).

Azevedo, A., Oliveira, A., Fortunato, A.B., Zhang, J., Baptista, A.M., A cross-scale numerical modeling system for management support of oil spill accidents, *Marine Pollution Bulletin*, 80, 02-Jan, pp. 132-147, 2014

The authors describe a 2D/3D oil spill modeling system addressing the distinct nature of the surface and water column fluids, major oil weathering and improved retention/reposition processes in coastal zones. The system integrates hydrodynamic, transport and oil weathering modules, which can be combined to offer different-complexity descriptions as required by applications across the river-to-ocean continuum. Features include accounting for different composition and rheology in the surface and water column mixtures, as well as spreading, evaporation, water-in-oil emulsification, shoreline retention, dispersion and dissolution.

Bacosa, H.P., Erdner, D.L., Liu, Z., Differentiating the roles of photooxidation and biodegradation in the weathering of Light Louisiana Sweet crude oil in surface water from the Deepwater Horizon site, *Marine Pollution Bulletin*, 95, 1, pp. 265-272, 2015a

The researchers determined the contributions of photooxidation and biodegradation to the weathering of Light Louisiana Sweet crude oil by incubating surface water from the Deepwater Horizon site under natural sunlight and temperature conditions. N-alkane biodegradation rate constants were about ten-fold higher than the photooxidation rate constants. For the 2-3 ring and 4-5 ring polycyclic aromatic hydrocarbons (PAHs), photooxidation rate constants were 0.08-0.98/day and 0.01-0.07/day, respectively.

The dispersant Corexit enhanced degradation of n-alkanes but not of PAHs. Compared to biodegradation, photooxidation increased transformation of 4-5 ring PAHs by 70% and 3-4 ring alkylated PAHs by 36%. Sunlight inhibited biodegradation of pristane and phytane, possibly due to inhibition of the bacteria that can degrade branched-alkanes.

Bacosa, H.P., Liu, Z., Erdner, D.L., Natural sunlight shapes crude oil-degrading bacterial communities in northern Gulf of Mexico surface waters, Frontiers in Microbiology, 6, DEC, p. 1325, 2015b

The researchers incubated surface water from the DWH site with addition of crude oil, Corexit dispersant, or both for 36 days under natural sunlight in the northern Gulf of Mexico. The bacterial community was analyzed over time for total abundance, density of alkane and polycyclic aromatic hydrocarbon degraders, and community composition via pyrosequencing. The results showed that, for treatments with oil and/or Corexit, sunlight significantly reduced bacterial diversity and evenness and was a key driver of shifts in bacterial community structure. In samples containing oil or dispersant, sunlight greatly reduced abundance of the Cyanobacterium Synechococcus but increased the relative abundances of Alteromonas, Marinobacter, Labrenzia, Sandarakinotalea, Bartonella, and Halomonas. Dark samples with oil were represented by members of Thalassobius, Winogradskyella, Alcanivorax, Formosa, Pseudomonas, Eubacterium, Erythrobacter, Natronocella, and Coxiella. Both oil and Corexit inhibited the Candidatus Pelagibacter with or without sunlight exposure. For the first time, they demonstrated the effects of light in structuring microbial communities in water with oil and/or Corexit.

Bagby, S.C., Reddy, C.M., Aeppli, C., Fisher, G.B., Valentine, D.L., Persistence and biodegradation of oil at the ocean floor following Deepwater Horizon, *Proceedings of the National Academy of Sciences of the United States of America*, 114, 1, pp. E9-E18, 2017

The authors assessed the compound-specific rates of biodegradation for 125 aliphatic, aromatic, and biomarker petroleum hydrocarbons that settled to the deep ocean floor following release from the Macondo well blowout. Based on study of up to 168 distinct hydrocarbon analytes in 2,980 sediment samples collected within 4 years of the Macondo spill.   They developed and identify a subset of 312 surficial samples consistent with contamination by Macondo oil. Three trends emerged from analysis of the biodegradation rates of 125 individual hydrocarbons in these samples. First, molecular structure served to effect biodegradation in a predictable fashion, with the simplest structures subject to fastest loss, indicating that biodegradation in the deep ocean progresses similarly to other environments. Second, for many alkanes and polycyclic aromatic hydrocarbons biodegradation occurred in two distinct phases, consistent with rapid loss while oil particles remained suspended, followed by slow loss after deposition to the seafloor. Third, the extent of biodegradation for any given sample was influenced by the hydrocarbon content, leading to substantially greater hydrocarbon persistence among the more highly contaminated samples. In other words, the more hydrocarbons, the less the biodegradation. In addition, under some conditions they found strong evidence for extensive degradation of numerous petroleum biomarkers, notably including the native internal standard 17α(H),21β(H)-hopane, commonly used to calculate the extent of oil weathering. This implies that work where only this hopane was used to perform studies may be in error.

The authors also speculate on the possible effect of dispersants on biodegradation. While it might appear that keeping the droplets suspended for longer in the water column would increase biodegradation, there is no evidence in this case that that was actually a fact in this case. Further, it was noted that there are studies showing some contrary evidence.

Bejarano, A.C., Mearns, A.J., Improving environmental assessments by integrating Species Sensitivity Distributions into environmental modeling: Examples with two hypothetical oil spills, *Marine Pollution Bulletin*, 93, 02-Jan, pp. 172-182, 2015

A three-dimensional trajectory model was used to simulate oil mass balance and environmental concentrations of two 795,000 L hypothetical oil spills modeled under physical and chemical dispersion scenarios. Species Sensitivity Distributions for Total Hydrocarbon Concentrations were developed, and Hazard Concentrations used as levels of concern. Potential consequences to entrained water column organisms were characterized by comparing model outputs with sensitivities, and obtaining the proportion of species affected and areas with oil concentrations exceeding 5% of hazard concentrations. Under the physically-dispersed oil scenario ≤77% of the oil remains on the water surface and strands on shorelines, while with the chemically-dispersed oil scenario ≤67% of the oil is entrained in the water column. For every 10% increase in chemical dispersion effectiveness, the average proportion of species affected and percent of hazard concentration increases, while shoreline oiling decreases. Integrating species sensitivity distributions into modeling may improve understanding of scales of potential impacts to water column organisms, and provide net environmental benefit comparison of oil spill response options.

Bejarano, A.C., Clark, J.R., Coelho, G.M., Issues and challenges with oil toxicity data and implications for their use in decision making: A quantitative review, *Environmental Toxicology and Chemistry*, 33, 4, pp. 732-742, 2014

The authors carry out a quantitative review to evaluate the use of standard toxicity testing data to help inform decisions regarding dispersant use, recognizing some key issues with current practices, specifically, reporting toxicity metrics (nominal vs measured), exposure duration (standard durations vs short-term exposures), and exposure concentrations (constant vs spiked). Analytical chemistry data were used to demonstrate the role of oil loading on acute toxicity and the influence of dispersants on chemical partitioning. The analyses presented here suggest that decisions should be made on the basis of measured aqueous exposure concentrations and preferably, using data from short-term exposure durations under spiked exposure concentrations.

Belkina, N., Sarkova, O., Jensen, S., Regulatory policies for using oil dispersants in the Barents Sea, Polar Research, 34, 2015, article no. 24326, 2015

The authors review the Joint Contingency Plan in the Barents Sea and any specific requirements for use of dispersants. The Plan emphasizes that in case of transboundary pollution the decision to use dispersants shall only be undertaken upon common agreement. The paper presents a comparison of the national regulatory approaches of Norway and Russia to using dispersants. The research is based on the analysis of legislative documents and interviews with oil companies, oil spill responders and relevant national authorities. The research reveals that in both countries use of dispersants requires preliminary authorization of the national agencies. In Norway, the pre-approval procedure and the algorithm of dispersants involvement in response to a real accident are clearly documented and are regularly tested. This has made the process of approval for using dispersants more efficient. In Russia, the lack of practical experience in using dispersants and well-established approval procedures can result in a long and unclear permitting process for each oil spill case. This could seriously hinder the use of dispersants to combat transboundary pollution in the Barents Sea, even if it is considered to be beneficial.

Belore, R., Wave tank dispersant effectiveness tests on Alaskan crude oils, *Proceedings of the 38th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 687-702, 2015

Several dispersant effectiveness tests using the SL Ross meso-scale tank on four Alaskan crude oils with four water salinities were conducted to examine the effectiveness of a marine dispersant over a range of water salinities under high energy breaking wave conditions. Alaska North Slope, Endicott, Northstar and Kuparuk crude oil were used in the testing. Tests were conducted on fresh, evaporated and evaporated plus emulsified crude oils. Tests were conducted in water with salinities of 5, 10, 20 and 30 ppt. All tests were conducted with a water temperature of 10 °C. Corexit 9500 was applied at a dispersant to oil ratio of 1:20 in all tests. The fresh oils were more effectively dispersed than the weathered oils that were more effectively dispersed than the weathered and emulsified oils. The most complete data sets collected were for the fresh oil tests. The results for the fresh oils indicate that the final dispersant effectiveness values are highest for the 30 ppt water and in all cases, drop as the test water salinity decreased to 5 ppt.

Benner, S.W., John, V.T., Hall, C.K., Simulation Study of Hydrophobically Modified Chitosan as an Oil Dispersant Additive, *Journal of Physical Chemistry B*, 119, 23, pp. 6979-6990, 2015

The authors perform a study of hydrophobically modified chitosan as a possible oil dispersant additive to reduce the volume of dispersant required in oil spill remediation. They present the results of discontinuous molecular dynamics simulations intended to determine how the HMC architecture affects its ability to prevent oil aggregation.

Bess, A., Young, L., Alternate prediction methods of laboratory dispersant effectiveness in the swirling flask test, 39th AMOP Technical Seminar on Environmental Contamination and Response, pp. 899-915, 2016

Bess and Young (2016) present several alternate methods for prediction of oil dispersibility in the US EPA swirling flask test using Corexit 9500 as well as a comparison with data for several other dispersants in the same test.

Beyer, J., Trannum, H.C., Bakke, T., Hodson, P.V., Collier, T.K., Environmental effects of the Deepwater Horizon oil spill: A review, *Marine Pollution Bullet*in, 110, 1, pp. 28-51, 2016

The authors review the biological effects of the DeepWater horizon spill including a brief review of the use of dispersants. Factors such as oil-biodegradation, ocean currents and response measures (dispersants, burning) reduced coastal oiling. Still, > 2100 km of shoreline and many coastal habitats were affected. Research shows that oiling caused a wide range of biological effects, although worst-case impact scenarios did not materialize in most cases. Biomarkers in individual organisms were more informative about oiling stress than population and community indices. Salt marshes and seabird populations were hard hit, but were also quite resilient to oiling effects. Monitoring demonstrated little contamination of seafood. Certain impacts are still understudied, such as effects on seagrass communities. Concerns of long-term impacts remain for large fish species, deep-sea corals, sea turtles and cetaceans.

Bhattacharya, D., Clement, T.P., Dhanasekaran, M., Evaluating the neurotoxic effects of Deepwater Horizon oil spill residues trapped along Alabama's beaches, *Life Sciences*, 155, pp. 161-166, 2016

The authors studied the in vitro cytotoxic effects of the chemicals trapped in tarmat fragments using hippocampal (neuron), kidney (nephron) and epithelial cells. Water accommodated fraction (WAF) of tarmat fragments was used in this study. Cytotoxicity was elucidated by the MTT assay and cellular morphology assessment. Markers of oxidative stress and apoptosis were assessed to study the toxicity effects. Tarmat WAF induced dose-dependent cellular toxicity. Chemicals trapped in tarmat WAF inhibited cell viability in the hippocampal, kidney and epithelial cells. Tarmat WAF also generated reactive oxygen species and increased activity of superoxide dismutase in hippocampal cells.

Bi, H., Si, H., Numerical simulation of oil spill for the Three Gorges Reservoir in China, *Water and Environment Journal*, 28, 2, pp. 183-191, 2014

A 3-D model is developed for the Three Gorges reservoir including natural and chemical dispersion.

Black, J.C., Welday, J.N., Buckley, B., Ferguson, A., Gurian, P.L., Mena, K.D., Yang, I., McCandlish, E., Solo-Gabriele, H.M., Risk assessment for children exposed to beach sands impacted by oil spill chemicals, *International Journal of Environmental Research and Public Health*, 13, 9, Article no. 853,2016

The authors evaluate the health risk to children who potentially contact beach sands impacted by oil spill chemicals (also chemicals in the oil) from the Deepwater Horizon disaster. To identify chemicals of concern, the U.S. Environmental Protection Agency's (EPA's) monitoring data collected during and immediately after the spill were evaluated. This dataset was supplemented with measurements from beach sands and tar balls collected five years after the spill. Of interest is that metals in the sediments were observed at similar levels between the two sampling periods; some differences were observed for metals levels in tar balls. Although PAHs were not observed five years later, there is evidence of weathered-oil oxidative by-products. Comparing chemical concentration data to baseline soil risk levels, three metals (As, Ba, and V) and four PAHs (benzo a pyrene, benz a anthracene, benzo b fluoranthene, and dibenz a,h anthracene) were found to exceed guideline levels prompting a risk assessment. For acute or sub-chronic exposures, hazard quotients, computed by estimating average expected contact behavior, showed no adverse potential health effects. For cancer, computations using 95% upper confidence limits for contaminant concentrations showed extremely low increased risk in the 10^{-6} range for oral and dermal exposure from arsenic in sediments and from dermal exposure from benzo a pyrene and benz a anthracene in weathered oil. Overall, results suggest that health risks are extremely low, given the limitations of available data. Limitations of this study are associated with the lack of toxicological data for dispersants and oil-spill degradation products. They also recommend studies to collect quantitative information about children's beach play habits, which are necessary to more accurately assess exposure scenarios and health risks.

Bodratti, A.M., Tsianou, M., Alexandridis, P., Surfactant-mineral interactions with applications in oil-spill dispersion and clean-up, *Engineering Sciences and Fundamentals 2014 - Core Programming Area at the 2014 AIChE Annual Meeting*, 2, pp. 1239-1247, 2014

These researchers show that the addition of surfactants increase the oil-mineral interactions resulting in more sedimentation.

Boglaienko, D., Tansel, B., Partitioning of fresh crude oil between floating, dispersed and sediment phases: Effect of exposure order to dispersant and granular materials, *Journal of Environmental Management*, 175, pp. 40-45,2016

Boglaienko and Tansel, (2016) analyzed the phase distribution of fresh floating Louisiana crude oil into dispersed, settled and floating phases depending on the exposure sequence to Corexit 9500A (dispersant) and granular materials. In artificial sea water at salinity 34‰. Limestone (2.00-0.300 mm) and quartz sand (0.300-0.075 mm) were used as the natural granular materials. Dispersant Corexit 9500A increased the amount of dispersed oil up to 33.76%. Addition of granular materials after the dispersant increased dispersion of oil to 47.96 %. When solid particles were applied on the floating oil before the dispersant, oil was captured as oil-particle aggregates and removed from the floating layer. However, dispersant addition led to partial release of the captured oil, removing it from the aggregate to the dispersed and floating phases. There was no visible oil aggregation with the granular materials when quartz or limestone was at the bottom of the flask before the addition of oil and dispersant. The results show that granular materials can be effective when applied from the surface for aggregating or dispersing oil. However, the granular materials in the sediments are not effective neither for aggregating nor dispersing floating oil.

Bookstaver, M., Bose, A., Tripathi, A., Interaction of Alcanivorax borkumensis with a surfactant decorated oil-water interface, *Langmuir*, 31, 21, pp. 5875-5881, 2015

Bookstaver et al. (2015) studied Alcanivorax borkumensis, a hydrocarbon degrading bacterium linked to oil degradation and its reaction to Corexit 9500. they built an experimental model to quantitatively measure the transient growth of Alcanivorax borkumensis at the interface of oil and water. This is the first study of how A. borkumensis interacts with a surfactant decorated oil-water interface. They used COREXIT EC9500A, cetylytrimethylamonium bromide, dioctyl sulfosuccinate sodium salt, l-α-phosphatidylcholine, sodium dodecyl sulfate, and Tween 20 to investigate the impact of dispersants on Alcanivorax borkumensis. They assessed the impact of these dispersants on the growth rate, lag time, and maximum concentration of Alcanivorax borkumensis. They show that the charge, structure, and surface activity of these surfactants greatly impact the growth of A. borkumensis. Their results indicated that out of the surfactants tested only Tween 20 assists Acanivorax borkumensis growth, the remaining ingredients slowed the growth of the bacterium.

Bostrom, A., Walker, A.H., Scott, T., Pavia, R., Leschine, T.M., Starbird, K., Oil Spill Response Risk Judgments, Decisions, and Mental Models: Findings from Surveying U.S. Stakeholders and Coastal Residents, *Human and Ecological Risk Assessment*, 21, 3, pp. 581-604, 2015

Bostrom et al. carried out a survey regarding oil spills. The study uses qualitative interview results and a response risk decision model to the design of a survey instrument. The decision model considers controlled burning, public health, and seafood safety. Surveying U.S. coastal residents (36,978 pairs of responses) through Google Insights identifies beliefs and gaps in understanding as well as related values and preferences about oil spills, and oil spill responses. A majority of respondents are concerned about economic impacts of major oil spills, and tend to see ocean ecosystems as fragile. They tend to see information about chemical dispersants as more important than ecological baseline information, and dispersants as toxic, persistent, and less effective than other response options. Although respondents regard laboratory studies as predictive of the effects of oil and of controlled burning, they are less confident that scientists agree on the toxicity and effectiveness of dispersants.

Bovenkamp-Langlois, L., Roy A., Determining the Sulfur species in the dispersants Corexit 9500A and 9527A applying S K-edge XANES spectroscopy, Journal of Physics: Conference Series, 712, 1, Paper no. 12093, 2016

Sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy was used to investigate the dispersants for the sulfur based components. The main sulfur containing component should be dioctyl sodium sulfosuccinate (DOSS). S K-edge XANES analysis shows that indeed the major sulfur species in both kinds of Corexit (9500A and 9527A) is sulfonic acid which is a part of DOSS. In addition, some fraction of sulfone was detected.

Bowers, R.R., Temkin, A.M., Guillette, L.J., Baatz, J.E., Spyropoulos, D.D., The commonly used nonionic surfactant Span 80 has RXRα transactivation activity, which likely increases the obesogenic potential of oil dispersants and food emulsifiers, *General and Comparative Endocrinology*, 238, pp. 61-68, 2016

Bowers et al. (2016) studied the Corexit-enhanced Water Accommodated Fraction (CWAF) of DWH crude oil which contains PPARγ transactivation activity, which is attributed to dioctyl sodium sulfosuccinate (DOSS), a probable obesogen. In addition to its use in oil dispersants, DOSS is commonly used as a stool softener and food additive. Because PPARγ functions as a heterodimer with RXRα to transcriptionally regulate adipogenesis, they investigated the potential of CWAF to transactivate RXRα and herein demonstrated that the Corexit component Span 80 has RXRα transactivation activity. Span 80 bound to RXRα in the low micromolar range and promoted adipocyte differentiation of 3T3-L1 preadipocytes. Further, the combination of DOSS and Span 80 increased 3T3-L1 adipocyte differentiation substantially more than treatment with either chemical individually, likely increasing the obesogenic potential of Corexit dispersants. From a public health standpoint, the use of DOSS and Span 80 as food additives heightens concerns regarding their use and mandates further investigations.

Brakstad, O.G., Nordtug, T., Throne-Holst, M., Biodegradation of dispersed Macondo oil in seawater at low temperature and different oil droplet sizes, *Marine Pollution Bulletin*, 93, 02-Jan, pp. 144-152, 2015

Brakstad et al. (2015) used a laboratory system to investigate biodegradation of small droplet oil dispersions (10 μm or 30 μm droplet sizes) of the Macondo oil premixed with Corexit 9500, using coastal Norwegian seawater at a low temperature (4-5 °C). Biotransformation of volatile and semivolatile hydrocarbons and oil compound groups was generally faster in the 10 μm than in the 30 μm dispersions, showing the importance of oil droplet size for biodegradation. These data therefore indicated that dispersant treatment to reduce the oil droplet size may increase the biodegradation rates of oil compounds.

Brandvik, P.J., Davies, E., Krause, D.F., Beynet, P.A., Agrawal, M., Evans, P., Subsea mechanical dispersion, adding to the toolkit of oil spill response technology, *Society of Petroleum Engineers - SPE International Conference and Exhibition on Health, Safety, Security, Environment, and Social Responsibility*, 2016a

Brandvik et al. (2016a) investigated other ways of reducing the effects of interfacial tension, other than use dispersants within a subsea oil plume, such as increasing the interfacial shear by introducing more turbulence within the rising oil plume. Using a combination of laboratory experimentation and computational fluid dynamics (CFD) they have explored the potential of three mechanisms-1) a rotating bladed shearing mixer, 2) ultrasonic cavitation and 3) high pressure water jetting. Physical experiments were conducted at the SINTEF Tower Basin facility in Norway. A scaled-down oil plume of Oseberg blend (1 L/min) was subjected to shear using commercially available rotating and ultrasonic devices both normally supplied for industrial mixing applications and adapted for operation within the tank. Results were compared to chemically dispersed oil under the same conditions. CFD modelling of water jetting was conducted using the BP High Performance Computer facility adopting a Volume of Fluid (VOF) multiphase model with advanced turbulence modelling and automated mesh refinement. Boundary conditions were set to replicate, as close as practical, the dimensions and physical properties used in the tank experiments. Results indicate that all three modes of increasing interfacial shear could be effective in dispersing oil. The ultrasonic device created a broad distribution of oil droplet sizes, spanning 10-100 μm in diameter whilst the mechanical shearing technique dispersed oil droplets into a narrower size distribution, centred on 16 μm. These values fall close to the droplet size of 70 μm dispersed using chemicals. Estimation of droplet sizes in the water jetting scenarios yielded values <50 μm. These tank scale experiments indicate that a new class of oil spill response technology may be possible using a mechanical device-Subsea Mechanical Dispersion.

Brandvik, P.J., Johansen, Ø., Davies, E.J., Leirvik, F., Krause, D.F., Daling, P.S., Dunnebier, D., Masutani, S., Nagamine, I., Storey, C., Brady, C., Bellore, R., Nedwed, T., Cooper, C., Ahnell, A., Pelz, O., Anderson, K., Subsea dispersant injection - Summary of operationally relevant findings from a multi-year industry initiative, *Society of Petroleum Engineers - SPE International Conference and Exhibition on Health, Safety, Security, Environment, and Social Responsibility*, 2016b

This paper presents data from a comprehensive set of laboratory experiments to evaluate the formation, fate, and transition of dispersed oil droplets in the water column during a subsea oil and gas blowout in combination with subsea dispersant injection. Many sub-sea well blowout oil and gas release scenarios form relatively large oil droplets (multiple millimeters), which then rapidly rise through the water column to form thick slicks on the ocean surface, potentially very near the source. On the other hand, smaller oil droplets (500 microns) rise more slowly and can stay suspended in the water column for days to weeks. Dispersant injection is therefore suggested to reduce the potential for floating oil and associated volatile hydrocarbons that may threaten worker health and safety, and reach ecologically and economically sensitive surface water and shoreline environments. The oil that disperses into the water column may pose temporary elevated exposures to organisms in the immediate area, but research and experience has shown that those exposures are rapidly mitigated by the effects of dilution and microbial degradation of the dispersed oil. The results of the laboratory studies, which examined the influence of different variables on the initial oil droplet size in an oil release scenario including oil release velocity, dispersant dosage, dispersant injection method, oil temperature, high pressure, gas-to-oil ratio, oil- and dispersant characteristics), revealed that dispersant injection is highly effective at reducing droplet size. The data also fit a new modified Weber Number scaling algorithm that can be used to calculate initial oil droplet size at field scales. Model simulations using the new modified Weber number scaling indicate that subsea dispersant injection can reduce droplet size by an order of magnitude which serves to delay and significantly reduce surfacing of oil from large oil spills.

Brasileiro, P.P.F., De Almeida, D.G., De Luna, J.M., Rufino, R.D., Dos Santos, V.A., Sarubbo, L.A., Optimization of biosurfactant production from Candida guiliermondii using a rotate central composed design, *Chemical Engineering Transactions*, 43, pp. 1411-1416, 2015

Brasileiro et al. (2015) propose biosurfactant production by Candida guilliermondii UCP 0992 grown in a low-cost medium and formulated with 4.0 % of corn steep, 2.5 % of molasses and 2.5 % of soybean residual oil carried out in a 1.2 L bioreactor, as an oil dispersant. The optimal levels of the variables were 250 rpm agitation speed, 132 h of cultivation time, 0.5 L/min of filtrated air and 4 % inoculum size. The experimental verifications allowed a maximum relative surface tension reduction to 31.45 mN/m and interface tension reduction to 9.04 mN/m, which was found to be equivalent to about 30.2 g/L isolated biosurfactant as estimated gravimetrically. Besides the optimization of operational parameters, the economic cost of € 22.37 was estimated to the biosurfactant produced according to the local price of the kWh. This work, therefore, showed that the fermentation time spent in flasks (144 h), could be reduced in 12 hours, increasing yield by 3.6 times. The biosurfactant produced by C. guilliermondii shows potential to be applied in oil spills.

Brazil, N., Nakhla, S., Kenny, S., Deployable oil dispersant system for fixed wing aircraft, *Oceans - St. John's, OCEANS 2014*, article no. 7003122, 2015

This paper outlines the structural design of an oil dispersant system on a Dash 8 Q300 aircraft, which can be deployed during flight. The system can be installed and ready within 6 hours of the accident, and the boom deployment fold-out will take less than two minutes.

Brenner, S., Oil spill modeling in the southeastern Mediterranean Sea in support of accelerated offshore oil and gas exploration, *Ocean Dynamics*, 65, 12, pp. 1685-1697, 2015

Brenner (2015) adapts the MEDSLIK oil spill model to the southern Mediterranean. The model accounts for time-dependent advection, dispersion, and physiochemical weathering of the surface slick. It is driven by currents produced by high-resolution dynamic downscaling of ocean reanalysis data and winds extracted from global atmospheric analyses. Worst case scenarios based on 30-day well blowouts under four sets of environmental conditions were simulated for wells located at 140, 70, and 20 km off the coast of central Israel. For the well furthest from the coast, the amount of oil remaining in the surface slick always exceeds the amount deposited on the coast. For the mid-distance well, the cases were evenly split. For the well closest to the coast, coastal deposition always exceeds the oil remaining in the slick. Additional simulations with the wind switched off helped highlight the importance of the wind in evaporation of the oil and in transporting the slick toward the southeastern coast.

Broje, V., Nedwed, T., API program to advance science of subsea dispersants use in oil spill response, *39th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 876-898, 2016

Broje et al. (2016) review oil spill response strategies for offshore spills including well control, natural attenuation, remote sensing, mechanical on-water recovery, dispersants used at the surface or subsea, in-situ burning, as well as shoreline protection and recovery. For offshore subsea releases, injection of dispersants subsea at a wellhead may offer significant benefits, including access to the freshest and non-emulsified oil in a high turbulence environment, ability to reduce the volume of required dispersant by injecting it directly into the oil stream, ability to safely operate day and night under a much wider range of weather conditions, and availability of a large water volume to rapidly decrease the concentration of a dispersed oil plume. To advance the science of subsea dispersant injection and provide a strong basis for inclusion of this technique into contingency plans the American Petroleum Institute (API) has sponsored research on various aspects of subsea dispersant injection for over 4 years. This comprehensive effort included studies on subsea dispersant injection effectiveness, oil fate and effects, subsea plume monitoring, and numerical modeling.

Burns, K.A., Jones, R., Assessment of sediment hydrocarbon contamination from the 2009 Montara oil blow out in the Timor Sea, *Environmental Pollution*, 211. pp. 214-225, 2016

Burns and Jones (2016) assess the sediment contamination from the blowout of the Montara H1 well (August. 2009) 260 km off the northwest coast of Australia resulting in the release of about 4.7 M L of light crude oil and gaseous hydrocarbons into the Timor Sea. Over the 74-day period of the spill, the oil remained offshore and did not result in shoreline incidents on the Australia mainland. At various times slicks were sighted over a 90,000 km^2 area, forming a layer of oil which was tracked by airplanes and satellites but the slicks typically remained within 35 km of the well head platform and were treated with 183,000 L of dispersants. The shelf area where the spill occurred is shallow (100-200 m) and includes off shore emergent reefs and cays and submerged banks and shoals. This study describes the increased inputs of oil to the system and assesses the environmental impact. Concentrations of hydrocarbon in the sediment at the time of survey were very low (total aromatic hydrocarbons (PAHs) ranged from 0.04 to 31 ng g-1) and were orders of magnitude lower than concentrations at which biological effects would be expected.

Buskey, E.J., White, H.K., Esbaugh, A.J., Impact of oil spills on marine life in the Gulf of Mexico: Effects on plankton, nekton, and deep-sea benthos, *Oceanography*, 29, 3, pp. 174-181, 2016

Buskey et al. (2016) review the extensive studies on the DeepWater Horizon spill to determine the potential acute and sublethal toxic effects of crude oil and dispersants on a range of planktonic, nektonic, and benthic marine organisms. Organisms such as phytoplankton, zooplankton, and fish were examined via controlled laboratory studies, while others, such as deep-sea benthic invertebrates, which are difficult to sample, maintain, and study in the laboratory, were assessed through field studies. Laboratory studies with marine fishes focused on the sublethal effects of oil and dispersants, and early life history stages were generally found to be more sensitive to these toxins than adults. Field studies in the vicinity of the DWH spill indicate a significant reduction in abundance and diversity of benthic meiofauna and macrofauna as well as visual damage to deep-sea corals. Overall, studies indicate that while the responses of various marine species to oil and dispersants are quite variable, a general picture is emerging that chemical dispersants may be more toxic to some marine organisms than previously thought, and that small oil droplets created by dispersant use and directly consumed by marine organisms are often more toxic than crude oil alone.

Cai, Q., Zhang, B., Chen, B., Cao, T., Lv, Z., Biosurfactant produced by a rhodococcus erythropolis mutant as an oil spill response agent, *Water Quality Research Journal of Canada*, 51, 2, pp. 97-105, 2016

Cai, Q., Zhang, B., Chen, B., Cao, T., Lv, Z., Bio-dispersant produced by a Rhodococcus erythropolis mutant as an oil spill response agent, *International Conference on Marine and Freshwater Environments, iMFE 2014*, 2014b

Cai et al. (2014b, 2016) reviewed biosurfactants as superior alternatives to currently used surfactants as they are generally more biodegradable, less toxic, and better at enhancing biodegradation. However, the application of biosurfactants is limited by the availability of economic biosurfactants and the corresponding producers that can work effectively. Hyperproducers generated by metabolic engineering of biosurfactant producers are highly desired to overcome this obstacle. A Rhodococcus erythropolis SB-1A strain was isolated from offshore oily water samples. One of its mutants derived by random mutagenesis with ultraviolet radiation, producing high levels of biosurfactants, was selected by the oil spreading technique. The mutant produces biosurfactants with critical micelle dilutions approximately four times those of the parent strain. The results obtained with thin layer chromatography indicated the produced biosurfactant remained unchanged between the mutant and the parent strain. In addition, the produced biosurfactants were recovered with solvent extraction and applied as the oil spill response agents. Based on the baffled flask test (BFT) results, the dispersion efficiency of the biosurfactants produced by the mutant is higher than that induced by the parent strain. When compared with Corexit dispersants, it was found that the produced biosurfactants performed better than Corexit 9527 and were comparable with Corexit 9500.

Cai, Q., Zhang, B., Chen, B., Li, P., Song, X., Zhu, Z., Behavior of Corexit dispersants in the Gulf of Mexico after the Deepwater Horizon oil spill, *International Conference on Marine and Freshwater Environments, iMFE 2014*, 2014b

Cai et al. (2014b) illustrate the transport and fate of the key ingredient of Corexit dispersants, dioctylsulfosuccinate, sodium salt (DOSS), in the Gulf of Mexico after the Deepwater Horizon oil spill. Relevant data were collected from literature and governmental databases. Subsequently, the distribution of DOSS was correlated with distributions of the flow of diverse hydrocarbons. The results indicated that DOSS had highest distribution correlation coefficients with gases and BTEX. The smaller molecular gases and aromatic compounds have higher distribution correlation coefficients while larger molecular alkanes have higher distribution correlation coefficients.

Cai, Z., Gong, Y., Liu, W., Fu, J., O'Reilly, S.E., Hao, X., Zhao, D., A surface tension based method for measuring oil dispersant concentration in seawater, *Marine Pollution Bulletin*, 109, 1, pp. 49-54, 2016

The group developed a new method to determine concentration of Corexit EC9500A, and likely other oil dispersants, in seawater. Based on the principle that oil dispersants decrease surface tension, a linear correlation was established between the dispersant concentration and surface tension. Thus, the dispersant concentration can be determined by measuring surface tension. The method could accurately analyze Corexit EC9500A in the concentration range of 0.5–23.5 mg/L. Minor changes in solution salinity (< 0.3%), pH (7.9–9.0), and dissolved organic matter (< 2.0 mg/L as TOC) had negligible effects on the measurements.

Cai, Z., Fu, J., Liu, W., Fu, K., O'Reilly, S.E., Zhao, D., Effects of oil dispersants on settling of marine sediment particles and particle-facilitated distribution and transport of oil components, *Marine Pollution Bulletin*, 114, 1, pp. 408-418, 2017

These researchers investigated the effects of three oil dispersants (Corexit EC9527A, Corexit EC9500A and SPC1000) on the settling of fine sediment particles and particle-facilitated distribution and transport of oil components in sediment-seawater systems. All three dispersants enhanced settling of sediment particles. The non-ionic surfactants (Tween 80 and Tween 85) play key roles in promoting particle aggregation. The effects varied with environmental factors (pH, salinity, DOM, and temperature). The strongest dispersant effect was observed at neutral or alkaline pH and in salinity range of 0–3.5 wt%. The presence of water accommodated oil and dispersed oil accelerated settling of the particles. Total petroleum hydrocarbons in the sediment phase were increased from 6.9% to 90.1% in the presence of Corexit EC9527A, and from 11.4% to 86.7% for PAHs.

Cappello, S., Genovese, M., Denaro, R., Santisi, S., Volta A., Bonsignore, M., Mancini, G., Giuliano, L., Genovese, L., Yakimov, M.M., Quick stimulation of Alcanivorax sp. By bioemulsificant EPS2003 on microcosm oil spill simulation, *Brazilian Journal of Microbiology,* 45, 4, pp. 1317-1323, 2014

Oil spill microcosms experiments were carried out to evaluate the effect of bioemulsificant exopolysaccharide (EPS2003) on quick stimulation of hydrocarbonoclastic bacteria. The early hours of oil spill, were stimulated using an experimental seawater microcosm, supplemented with crude oil and EPS2003; this system was monitored for 2 days and compared to control microcosm (only oil-polluted seawater). Determination of bacterial abundance, heterotrophic cultivable and hydrocarbon-degrading bacteria were carried out. Community composition of marine bacterioplankton was determined by 16S rRNA gene clone libraries. Data obtained indicated that bioemulsificant addition stimulated an increase of total bacterial abundance and, in particular, selection of bacteria related to Alcanivorax genus; confirming that EPS2003 could be used for the dispersion of oil slicks and could stimulate the selection of marine hydrocarbon degraders thus increasing bioremediation process.

Chan, G.K.Y., Chow, A.C., Adams, E.E., Effects of droplet size on intrusion of sub-surface oil spills, *Environmental Fluid Mechanics*, 15, 5, pp. 959-973, 2015

The researchers the effects of droplet size on droplet intrusion and subsequent transport in sub-surface oil spills. In an inverted laboratory set-up, negatively buoyant glass beads were released continuously into a quiescent linearly stratified system to simulate buoyant oil droplets in a rising multiphase plume. Settled particles collected from the bottom of the tank exhibited a radial Gaussian distribution, consistent with having been vertically well mixed in the intrusion layer, and a spatial variance that increased monotonically with decreasing particle size. A new typology was proposed to describe plume structure based on the normalized particle slip velocity. An analytical model assuming well-mixed particle distributions within the intrusion layer was derived to predict the standard deviation of the particle distribution, and predictions were found to agree well with experimental values. Experiments with beads of multiple sizes also suggested that the interaction between two particle groups had minimal effect on their radial particle spread. Because chemical dispersants have been used to reduce oil droplet size, this study contributes to one measure of dispersant effectiveness. Results are illustrated using conditions taken from the 'Deep Spill' field experiment and the recent Deepwater Horizon oil spill.

Chen, Y., Reese, D.H., Corexit-EC9527A disrupts retinol signaling and neuronal differentiation in P19 embryonal pluripotent cells, *PLoS ONE*, 11, 9, article no. e0163724, 2016

The authors study Retinol (vitamin A) signaling, mediated by all-trans retinoic acid (RA), which is essential for neural tube formation and the development of many organs in the embryo. The physiological levels of RA in cells and tissues are maintained by the retinol signaling pathway (RSP), which controls the biosynthesis of RA from dietary retinol and the catabolism of RA to polar metabolites for removal. RA is a potent activating ligand for the RAR/RXR nuclear receptors. Through RA and the receptors, the RSP modulates the expression of many developmental genes; interference with the RSP is potentially teratogenic. In this study, the mouse P19 embryonal pluripotent cell, which contains a functional RSP, was used to evaluate the effects of the Corexit dispersants on retinol signaling and associated neuronal differentiation. The results showed that Corexit-EC9500A was more cytotoxic than Corexit-EC9527A to P19 cells. At non-cytotoxic doses, Corexit-EC9527A inhibited retinol-induced expression of the Hoxa1 gene, which encodes a transcription factor for the regulation of body patterning in the embryo. Such inhibition was seen in the retinol- and retinal- induced, but not RA-induced, Hoxa1 up-regulation, indicating that the Corexit chemicals primarily inhibit RA biosynthesis from retinal. In addition, Corexit-EC9527A suppressed retinol-induced P19 cell differentiation into neuronal cells, indicating potential neurotoxic effect of the chemicals under the tested conditions. The surfactant ingredient, dioctyl sodium sulfosuccinate (DOSS), may be a major contributor to the observed effect of Corexit-EC9527A in the cell.

Chopra, A., Coolbaugh, T.S., Recent technology advances for effective oil spill response, *39th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 760-783, 2016

This is a review of new oil spill technology with emphasis on sub-sea dispersant application. Included are: Mechanical Containment and Recovery: Enhancements have been implemented recently, e.g., higher efficiency skimmers, booms that function in faster currents, systems that allow for more efficient boom deployment in open water and in rivers and temporary portable under-flow dams for inland responses. In Situ Burning: New booming systems have been developed and the effective operational use of ISB has been demonstrated. Dispersants: The ability to use dispersants at depth provides an opportunity to treat a spill as close to the source as possible, thereby making it possible to use less product than might be needed to treat a surface slick. Surveillance, Monitoring and Targeting the Areas of Thickest Oil: A key aspect of an effective response is the ability to identify the location of the thickest part of a slick, since it is often the case that the majority of the slick volume resides in a relatively small part of the area. By identifying the areas of thicker oil, it is possible to deploy response tools to those areas specifically in order to significantly increase their encounter rate.

Ciaralli, F., Avezzano Comes, F., Dispersant: Cleaning composition for use as dispersant for oil spills or as surface washing agent to enhance oil removal from substrates, *Petroleum Abstracts*, 56,16, p. 107, 2016

The author proposes a concentrated, improved formulation effective for dispersing oil or for washing oil-contaminated substrates. The formulation contains a mixture of chemical surfactants and a solvent system, e.g., glycol, glycol ether, H_2O, and an inorganic alkali metal halide.

Committee on the Effects of the Deepwater Horizon Mississippi Canyon-252 Oil Spill on Ecosystem Services in the Gulf of Mexico, Ocean Studies Board, Division on Earth and Life Studies, National Research Council: An ecosystem services approach to assessing the impacts of the DeepWater horizon oil spill in the Gulf of Mexico, *National Academy Press*, Washington, DC, 235 pp., 2014

This is a general survey of the impacts of the DeepWater Horizon spill. The committee's findings are summarized as: The overall impacts in the Gulf of Mexico (GoM) wetlands can be summarized as follows: *Marshes* -

• Acute effects on marshes, where the biota are not expected to recover, appear to be confined to the edges of bays, canals, and creeks in a limited subset of the oiled wetlands.

• Where the vegetation has died and the root systems have been lost in heavily oiled areas, the erosion of sediment is leading to the conversion of once productive marshland to open water.

• Subsequent tropical storm activity resulted in additional erosion of oiled marshes.

• Based on numerous studies that document a rapid recovery from oiling and a relatively low sensitivity of perennial marsh vegetation to hydrocarbons, GoM marsh vegetation can be expected to suffer little or no long-term impairment from the DWH oil spill in areas where roots and rhizomes survived the initial impact of oil fouling. If roots and rhizomes did not survive, then an area will not recover on its own.

Fisheries - Impacts on fishery productivity from oil spills and other stressors are not as well understood. Despite long-term studies and ongoing development of models, the ability to detect spatial and temporal differences in fishery productivity in the GoM is limited.

Marine Mammals – Dolphins - As apex predators, the dolphins' health and well-being serve as important indicators of the health of the GoM and oceans in general. Their position as the most studied and arguably the most popular and charismatic marine mammal makes them a centerpiece for conservation science, education, and ecotourism. The stranding of hundreds of dolphins in the GoM during, and especially after the DWH oil spill have stimulated considerable public concern. If the recent mortality event is determined to be linked to the DWH oil spill, then an opportunity may exist to establish a plan to protect and restore the dolphin habitat as well to reduce dolphin mortality due to human activities.

Other Findings

Finding 4.1. Chemical dispersants have long been applied to oil spills to break up oil into smaller droplets. From a purely physical perspective, chemical oil dispersants can reduce oil concentrations at the surface by increasing horizontal and vertical mixing of the oil. This tends to enhance biodegradation and mitigate the adverse effects of the oil at the surface including the reduction of vapors (thus enhancing the safety of response personnel). However, the overall volume of ocean impacted by the oil will increase, which may have adverse effects especially for subsurface biota.

Finding 4.2. Existing studies of the biodegradation rate of dispersants alone show that they do degrade, although at rates that depend strongly on the concentration of dissolved oxygen and the composition of the surfactant. The biodegradation rate of chemically dispersed oil can also vary widely, but some, if not all, of this variation reflects the lack of realism in the underlying experiments. Further studies are needed that use realistic initial dispersed oil concentrations and avoid boundary effects that increase oil-dispersant concentrations.

Finding 4.3. There is some evidence that chemically dispersed oil and some dispersant compounds are toxic to some marine life, especially those in early life stages. There is contradictory evidence as to whether chemically dispersed oil is more or equally toxic to marine life compared to undispersed oil. The use of dispersants does reduce the amount of oil available to reach shorelines and shallow water environments and impact additional marine life. These facts may be weighed when considering the net environmental benefit to having used dispersants to respond to the DWH oil spill.

Finding 4.4. The use of dispersants helped to keep an estimated 500,000 barrels of the oil away from the highly productive and sensitive coastal areas. The use of chemical dispersants was controversial from a public point of view because of concerns about dispersant toxicity, the potential for dispersants to make oil more bioavailable (thus making dispersed oil more toxic than non-dispersed oil), and the persistence of dispersants, dispersed oil, or dispersant by-products. The long-term impacts of dispersants and dispersed oil from the DWH spill on the food web and other ecosystem services of the GoM are still undetermined, and additional research is necessary in this area.

Finding 4.5. Several technical innovations led to in situ burning being the most successful response method in terms of removing oil from the sea surface offshore (estimated to be as high as 300,000 barrels or 6 percent of the total volume of oil spilled) and thus keeping oil away from sensitive coastal habitats. Although black particulate carbon clouds were clearly visible and subsistence consumers of local fish may have had a slight increase in the risk of cancer (1:1 million), there are no other documented negative impacts at this time. Further long-term research is needed to continue to look for future potential impacts.

Finding 4.6. Skimmers can be an effective means of recovering oil with little impact on the environment. However, given the diluted and dispersed nature of the DWH oil spill, skimmers were only able to capture between 75,000 to 300,000 barrels of oil. Nonetheless, skimming prevented this oil from reaching sensitive coastal ecosystems and impacting the services they provide.

Finding 4.7. The effectiveness of mechanisms for near-shore and onshore protection of shorelines was negligible in terms of berms and freshwater diversions, but somewhat effective in terms of booms. Well-formed scientific advice was provided in advance that sand berms and diversions would be ineffective in keeping the oil from reaching the wetlands. Moving forward, decision analyses may be needed to refine guidelines and to optimize the effectiveness of various technologies and protocols. Additional research is needed to monitor the overall impacts of these response technologies on ecosystems and the services they provide.

Finding 4.8. The impacts of shoreline cleanup operations have not yet been determined. Cleanup efforts were inconsistently successful because of storms, shifting sediments, variable beach habitats, and variable oiling profiles along the northern GoM coasts. Lightly oiled beaches on barrier islands were the easiest to clean and restore.

Finding 4.9. Abiotic weathering processes and microbial degradation are major processes controlling the eventual removal of oil that enters marine and coastal environments. Thus, natural attenuation of some oil will occur without technological interventions.

Finding 4.10. The fate and transformations of oil from the DWH oil spill were and will continue to be influenced by natural attenuation processes. These processes may be considered the best practical methods for oil removal in sensitive habitats, where the application of technology may cause more harm, or in logistically inaccessible habitats. Continued observations, monitoring, and research of these processes, especially in relation to technological countermeasures, are warranted.

Finding 4-11. Any conclusive assessment of the impacts of response technologies on the GoM marine ecosystem and ecosystem services would be premature at this time, given the amount of key data and analyses that is being held confidentially in the ongoing NRDA process. Nonetheless, the committee believes that the technologies applied offshore mitigated the impacts of the oil spill on sensitive coastal habitats. A further factor for consideration is that only 3 years have passed since the spill started, and many substantial impacts may not become apparent for several more years.

Coolbaugh, T., Cox, R., Development of a bench scale effectiveness test for subsea dispersant use: An oil spill response joint industry project of the international association of oil and gas producers and IPIECA, *Proceedings of the 38th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 703-714, 2015

A Research project was initiated with two international organizations (SINTEF and CEDRE) to develop in parallel an approach to gaining a better understanding of subsea dispersant use. The objective was to validate the hypothesis that subsea dispersant injection allows for effective dispersion both in high and low energy situations. Uncertainty exists concerning the dispersion mechanism for subsea application and how physical/chemical parameters, such as the concentration of dispersants, type of oil and dispersant, affect the process. Another key variable is the energy involved during a blow-out and the extent to which variations in mixing energy contribute to dispersion efficiency and the opportunity to reduce DOR in subsea application versus surface application.

Cornwall, W., Critics question plans to spray dispersant in future deep spills, *Science*, 348, 6230, p. 27, 2015

This is a comment article written in Science which quotes several experts on the efficacy of the DeepWater Horizon subsea injection and further use of it.

Crisafi, F., Genovese, M., Smedile, F., Russo, D., Catalfamo, M., Yakimov, M., Giuliano, L., Denaro, R., Bioremediation technologies for polluted seawater sampled after an oil-spill in Taranto Gulf (Italy): A comparison of biostimulation, bioaugmentation and use of a washing agent in microcosm studies, *Marine Pollution Bulletin*, 106, 02-Jan, pp. 119-126, 2016

The authors have investigated the effect of three treatments in oily-seawater after a real oil-spill in the Gulf of Taranto, Italy. Biostimulation with inorganic nutrients allowed the biodegradation of the 73 % of hydrocarbons, bioaugmentation with a selected hydrocarbonoclastic consortium consisting of Alcanivorax borkumensis, Alcanivorax dieselolei, Marinobacter hydrocarbonoclasticus, Cycloclasticus sp. 78-ME and Thalassolituus oleivorans degraded 79 %, while the addition of nutrients and a washing agent has allowed the degradation of the 69 %. On the other hand, microbial community was severely affected by the addition of the washing agent and the same product seemed to inhibit the growth of the majority of strains composing the selected consortium at the tested concentration. The use of dispersant should be accurately evaluated also considering its effect on the principal biodegradation species.

Cuny, P., Gilbert, F., Militon, C., Stora, G., Bonin, P., Michotey, V., Guasco, S., Duboscq, K., Cagnon, C., Jézéquel, R., Cravo-Laureau, C., Duran, R., Use of dispersant in mudflat oil-contaminated sediment: behavior and effects of dispersed oil on micro- and macrobenthos, *Environmental Science and Pollution Research*, 22, 20, pp. 15370-15376, 2015

The authors studied mudflat sediments, maintained during 286 days in mesocosms, were contaminated or not with Ural blend crude oil (REBCO) and treated or not with dispersant (Finasol OSR52). While the dispersant did not lead to an increase of hydrocarbon biodegradation, its use enables an attenuation of more than 55 % of the sediment concentration of total petroleum hydrocarbons. Canonical correspondence analysis (CCA) correlating T-RFLP patterns with the hydrocarbon content and bacterial abundance indicated weak differences between the different treatments except for the mesocosm treated with oil and dispersant for which a higher bacterial biomass was observed. The use of the dispersant did not significantly decrease the macrobenthic species richness or macroorganisms' densities in uncontaminated or contaminated conditions. However, even if the structure of the macrobenthic communities was not affected, when used in combination with oil, biological sediment reworking coefficient was negatively impacted. The use of the dispersant should consider, long-term effects on functional aspects of the benthic system such as bioturbation and bacterial activity.

Dailey, D., Starbird, K., "It's raining dispersants": Collective sensemaking of complex information in crisis contexts, *Proceedings of the ACM Conference on Computer Supported Cooperative Work, CSCW*, 2015-January, pp. 155-158, 2015

To make sense of the BP DeepWater Horizon, oil spill people had to grapple with uncertain and sometimes contentious, complex information. This empirical study shows that an emergent, connected crowd interacted to surface, share, question and discuss these complexities. While studies have observed collective sense-making taking place via social media in other kinds of crises, this study extends the understanding of emergent crowd work as collective sense-making where members of the public assemble and interpret evidence on complex topics in a crisis context, perhaps performing a kind emergent citizen science.

Daly, K.L., Passow, U., Chanton, J., Hollander, D., Assessing the impacts of oil-associated marine snow formation and sedimentation during and after the Deepwater Horizon oil spill, *Anthropocene*, 13, pp. 18-33, 2016

The authors summarize marine snow formation, incorporation of oil, and subsequent gravitational settling to the seafloor (i.e., MOSSFA: Marine Oil Snow Sedimentation and Flocculent Accumulation) was a significant pathway for the distribution and fate of oil in the case of the DeepWater Horizon, accounting for as much as 14% of the total oil released. Long residence times of oil on the seafloor will result in prolonged exposure by benthic organisms and economically important fish. Bioaccumulation of hydrocarbons into the food web also has been documented. Major surface processes governing the MOSSFA event included an elevated and extended Mississippi River discharge, which enhanced phytoplankton production and suspended particle concentrations, zooplankton grazing, and enhanced microbial mucus formation. Previous reports indicated that MOS sedimentation also occurred during the Tsesis and Ixtoc-I oil spills; thus, MOSSFA events may occur during future oil spills, particularly since 85% of global deep-water oil exploration sites are adjacent to deltaic systems. They provide a conceptual framework of MOSSFA processes and identify data gaps to help guide current research and to improve the ability to predict MOSSFA events under different environmental conditions.

Dambros, J.W.V., Marques, W.C., Stringari, C.E., Evaluation of the numerical method runge-kutta used in the oil dispersion ECOS model [Avaliação da implementação do método numérico de runge-kutta ao modelo de dispersão do óleo ECOS], *Proceedings - 2014 Symposium on Automation and Computation for Naval, Offshore and Subsea, NAVCOMP 2014*, 7469509, pp. 38-41, 2014

The researcher model vertical dispersion and sedimentation. The numerical model developed at the Universidade Federal do Rio Grande (ECOS - Easy Coupling Oil System) is constantly modified in order to improve the simulations and make the results similar to real scenarios. The group uses the numerical method Runge-Kutta to solve the differential equations and compare the results with the Euler method previously used by this model. The presented results indicate that there are a few differences in the displacement of the oil slick between the simulations where the Runge-Kutta of second and fourth order were employed. However, there is a high variation when these methods are compared with the Euler method which the oil are spreading more rapidly.

Dasgupta, S., Huang, I.J., McElroy, A.E., Hypoxia enhances the toxicity of Corexit EC9500A and chemically dispersed Southern Louisiana Sweet Crude Oil (MC-242) to sheepshead minnow (Cyprinodon variegatus) larvae, *PLoS ONE*, 10, 6, e0128939, 2015

Dasgupta et al. (2015) evaluated the effects of short term (48 hr) exposures to Corexit EC9500A, water accommodated fractions (WAF), and chemically enhanced water accommodated fractions (CEWAF) prepared from Southern Louisiana Sweet Crude Oil (MC 242) on survival of sheepshead minnow (Cyprinodon variegatus) larvae held under normoxic (ambient air) or hypoxic (2 mg/L O_2) conditions. Results demonstrated that hypoxia significantly enhances mortality observed in response to Corexit or CEWAF solutions. In the latter case, significant interactions between the two stressors were also observed. The data support the need to further evaluate the combined stresses imparted by hypoxia and exposure to petroleum hydrocarbons and dispersants.

DeLeo, D.M., Ruiz-Ramos, D.V., Baums, I.B., Cordes, E.E., Response of deep-water corals to oil and chemical dispersant exposure, *Deep-Sea Research Part II: Topical Studies in Oceanography*, 129, pp. 137-147, 2016

This study examined the effects of bulk oil-water mixtures, water-accommodated oil fractions, the dispersant Corexit 9500A, and the combination of hydrocarbons and dispersants on three species of corals living near the spill site in the Gulf of Mexico between 500 and 1100 m depths: Paramuricea type B3, Callogorgia delta and Leiopathes glaberrima. Following short-term toxicological assays (0-96 h), all three coral species examined showed more severe health declines in response to dispersant alone (2.3-3.4 fold) and the oil-dispersant mixtures (1.1-4.4 fold) than in the oil-only treatments. Higher concentrations of dispersant alone and the oil-dispersant mixtures resulted in more severe health declines. C. delta exhibited somewhat less severe health declines than the other two species in response to oil and oil/dispersant mixture treatments, likely related to its increased abundance near natural hydrocarbon seeps. These experiments provide direct evidence for the toxicity of both oil and dispersant on deep-water corals.

DeLorenzo, M.E., Eckmann, C.A., Chung, K.W., Key, P.B., Fulton, M.H., Effects of salinity on oil dispersant toxicity in the grass shrimp, Palaemonetes pugio, *Ecotoxicology and Environmental Safety*, 134, pp. 256-263, 2016

This study examined the effects of salinity on the toxicity of two oil dispersants, Corexit 9500 and Finasol OSR 52. The grass shrimp, *Palaemonetes pugio*, was used as a test species. It is a euryhaline species that tolerates salinities from brackish to normal seawater. Adult and larval life stages were tested with each dispersant at three salinities, 5, 20, and 30 ppt. Median acute lethal toxicity thresholds and oxidative stress responses were determined. The toxicity of both dispersants was significantly influenced by salinity, with greatest toxicity observed at the lowest salinity tested. Larval shrimp were significantly more sensitive than adult shrimp to both dispersants, and both life stages were significantly more sensitive to Finasol than to Corexit (toxicities varied from 17 to 447 mg/L depending on salinity, life stage and dispersant). Oxidative stress in adult shrimp, as measured by increased lipid peroxidation activity, occurred with exposure to both dispersants.

Demopoulos, A.W.J., Bourque, J.R., Cordes, E., Stamler, K.M., Impacts of the Deepwater Horizon oil spill on deep-sea coral-associated sediment communities, *Marine Ecology Progress Series*, 561, pp. 51-68, 2016

In 2011, sediments were collected adjacent to several coral habitats located 6 to 183 km from the wellhead in order to quantify the extent of impact of the DWH spill on infaunal communities. Higher variance in macrofaunal abundance and diversity, and different community structure (higher multivariate dispersion) were associated with elevated hydrocarbon concentrations and contaminants at sites closest to the wellhead, consistent with impacts from the spill. In contrast, variance in meiofaunal diversity was not significantly related to distance from the wellhead and no other community metric (e.g. density or multivariate dispersion) was correlated with contaminants or hydrocarbon concentrations. Concentrations of polycyclic aromatic hydrocarbons (PAH) provided the best statistical explanation for observed macrofaunal community structure, while depth and presence of fine-grained mud best explained meiofaunal community patterns. Impacts associated with contaminants from the DWH spill resulted in a patchwork pattern of infaunal community composition, diversity, and abundance, highlighting the role of variability as an indicator of disturbance.

De Serio, F., Mossa, M., Assessment of hydrodynamics, biochemical parameters and eddy diffusivity in a semi-enclosed Ionian basin, *Deep-Sea Research Part II: Topical Studies in Oceanography*, 133, pp. 176-185, 2016

De Serio and Mossa (2016) used monthly surface current data in the Ionian Sea to obtain time-averaged values of the turbulent velocity components, turbulent kinetic energy and turbulent time scales. Based on these calculated turbulent parameters, the horizontal eddy diffusivity was computed with the hypothesis of homogeneous turbulence using two methods, which provided results with the same order of magnitude. These results are of interest for numerical dispersion models. Finally, only referring to the month of December 2014, the time series of the crude oil concentration was available at the station and was examined in depth. The field data enabled them to conclude that the crude oil dispersion process is influenced by the sea turbulence.

Dussauze, M., Camus, L., Le Floch, S., Lemaire, P., Theron, M., Pichavant-Rafini, K., Effect of dispersed oil on fish cardiac tissue respiration: A comparison between a temperate (dicentrarchus labrax) and an Arctic (boreogadus saida) species, *Proceedings of the 37th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 482-493, 2014

Dussauze et al. (2014) compared the impact on tissue respiration of a dispersed oil (weathered Arabian Light) on two fish species, sea bass (Dicentrarchus labrax) and polar cod (Boreogadus saida) representative respectively of temperate and Arctic water ecosystems. Polar cod and sea bass were exposed for 48 hours to one of the following treatments: control, mechanically dispersed oil. chemically dispersed oil and dispersant alone. The impacts of these exposure conditions were assessed by heart energy metabolism using respirometry on permeabilized cardiac fibers. Following exposure, alteration in measurements of O_2 consumption by permeabilized cardiac fibers was found for the two species. The results show that for polar cod, oil alone decreased the activity of the respiratory chain whereas the dispersant alone did not have any impact. For sea bass, the results were different, dispersant alone decreased the activity of the respiratory chain whereas the results for oil alone were not different from the control group. These results show that oil and dispersants can alter mitochondrial activity.

Dussauze, M., Danion, M., Floch, S.L., Lemaire, P., Theron, M., Pichavant-Rafini, K., Growth and immune system performance to assess the effect of dispersed oil on juvenile sea bass (Dicentrarchus labrax), *Ecotoxicology and Environmental Safety*, 120, pp. 215-222, 2015a

Juvenile sea bass were exposed for 48 h to dispersed oil (mechanically and chemically) or dispersants alone. The impact of these exposure conditions was assessed using growth and immunity. The increase observed in polycyclic aromatic hydrocarbon metabolites in bile indicated oil contamination in the fish exposed to chemical and mechanical dispersion of oil without any significant difference between these two groups. After 28 days of exposure, no significant differences were observed in specific growth rate, apparent food conversion efficiency and daily feeding). Following the oil exposure, fish immunity was assessed by a challenge with Viral Nervous Necrosis Virus (VNNV). Fish mortality was observed over a 42-day period. After 12 days post-infection, cumulative mortality was significantly different between the control group (16% $p \leq 0.05$) and the group exposed to chemical dispersion of oil (30% $p \leq 0.05$). However, at the end of the experiment, no significant difference was recorded in cumulative mortality or in VNNV antibodies secreted in fish in responses to the treatments. These data suggested that in the experimental condition, following the oil exposure, sea bass growth was not affected whereas an impact on immunity was observed during the first days. However, this effect on the immune system did not persist over time.

Dussauze, M., Danion, M., Le Floch, S., Lemaire, P., Pichavant-Rafini, K., Theron, M., Innate immunity and antioxidant systems in different tissues of sea bass (Dicentrarchus labrax) exposed to crude oil dispersed mechanically or chemically with Corexit 9500,Ecotoxicology and Environmental Safety, 120, pp. 270-278, 2015b

Dussauze et al. (2015b) evaluated effects of chemically dispersed oil by the dispersant Corexit 9500 on innate immunity and redox defenses in sea bass (Dicentrarchus labrax). The fish were exposed 48 h to four experimental conditions: a control group, a group only exposed to the dispersant (3.6. mg/L) and two groups exposed to 80 mg/L oil mechanically or chemically dispersed. Alternative pathway of complement activity and lysozyme concentration was measured in plasma in order to evaluate the general fish health status. Total glutathione, glutathione peroxidase (GPX) and superoxide dismutase (SOD) were analyzed in gills, liver, brain, intestine and muscle. The chemical dispersion induced a significant reduction of lysozyme concentration when compared to the controls, and the hemolytic activity of the alternative complement pathway was increased in mechanical and chemical dispersion. The analysis of SOD, GPX and total glutathione showed that antioxidant defenses were activated in liver and reduced in intestine and brain. Dispersant was also responsible for an SOD activity inhibition in these two last tissues, demonstrating a direct effect of this dispersant on reactive oxygen species homeostasis that can be interpreted as a signal of tissue toxicity. This result raised concerns about the use of dispersants and show that they can lead to adverse effects on marine species.

Dussauze, M., Pichavant-Rafini, K., Le Floch, S., Lemaire, P., Theron, M., Acute toxicity of chemically and mechanically dispersed crude oil to juvenile sea bass (Dicentrarchus labrax): Absence of synergistic effects between oil and dispersants, *Environmental Toxicology and Chemistry*, 34, 7, pp. 1543-1551, 2015c

Dussauze et al. (2015c) assessed the relative acute toxicities of mechanically and chemically dispersed oil (crude Arabian Light) in controlled conditions. Juvenile sea bass (Dicentrarchus labrax) were exposed to 4 commercial formulations of dispersants (Corexit EC9500A, Dasic Slickgone NS, Finasol OSR 52, Inipol IP 90), to mechanically dispersed oil, and to the corresponding chemical dispersions. Acute toxicity was evaluated at 24 h, 48 h, 72 h, and 96 h through the determination of 10%, 50%, and 90% lethal concentrations calculated from measured total petroleum hydrocarbon (TPH) concentrations; Kaplan-Meyer mortality analyses were based on nominal concentrations. Fish were exposed to the dissolved fraction of the oil and to the oil droplets (ranging from 14.0 μm to 42.3 μm for the chemical dispersions). Kaplan-Meyer analyses demonstrated an increased mortality in the case of chemical dispersions. This difference can be attributed mainly to differences in TPH, because the chemical lethal concentrations were not reduced compared with mechanical lethal concentrations (except after 24 h of exposure). The ratios of lethal concentrations of mechanical dispersions to the different chemical dispersions were calculated to allow direct comparisons of the relative toxicities of the dispersions. The results ranged from 0.27 to 3.59 (mechanical to chemical), with a mean ratio close to 1 (0.92). These results demonstrate an absence of synergistic effect between oil and chemical dispersants.

Dussauze, M., Pichavant-Rafini, K., Belhomme, M., Buzzacott, P., Privat, K., Le Floch, S., Lemaire, P., Theron, M., Dispersed oil decreases the ability of a model fish (Dicentrarchus labrax) to cope with hydrostatic pressure, *Environmental Science and Pollution Research*, 24, 3, pp. 1-9, 2016

Dussauze et al. (2017) evaluated pressure challenge as an assessment of consequences of chemically dispersed oil, followed by a high hydrostatic pressure challenge. This work was conducted on juvenile Seabass, *Dicentrarchus labrax*. Seabass were exposed for 48 h to dispersant alone (nominal concentration (NC) = 4 mg L^{-1}), mechanically dispersed oil (NC = 80 mg L^{-1}), two chemically dispersed types of oil (NC = 50 and 80 mg L^{-1} with a dispersant/oil ratio of 1/20), or kept in clean seawater. Fish were then exposed for 30 min at a simulated depth of 1350 m, corresponding to pressure of 136 absolute atmospheres (ATA). The probability of fish exhibiting normal activity after the pressure challenge significantly increased from 0.40 to 0.55 when they were exposed to the dispersant but decreased to 0.26 and 0.11 in the case of chemical dispersion of oil (at 50 and 80 mg L⁻1, respectively). The chemical dispersion at 80 mg L^{-1} also induced an increase in probability of death after the pressure challenge (from 0.08 to 0.26). This study clearly demonstrates the ability of a pressure challenge test to show the effects of a contaminant on the capacity of fish to face hydrostatic pressure.

Echols, B.S., Smith, A.J., Gardinali, P.R., Rand, G.M., Acute aquatic toxicity studies of Gulf of Mexico water samples collected following the Deepwater Horizon incident (May 12, 2010 to December 11, 2010), *Chemosphere*, 120, pp. 131-137, 2015

Echols et al. (2015) evaluated waters from the Deepwater Horizon MC-252 incident for toxicity using Americamysis bahia, Menidia beryllina and Vibrio fischeri (Microtox assay). Organisms were exposed to GOM water samples collected in May-December 2010. Samples were collected where oil was visibly present on the water surface or the presence of hydrocarbons at depth was indicated by fluorescence data or reduced dissolved oxygen. Toxicity tests were conducted using water-accommodated fractions (WAFs), and oil-in-water dispersions (OWDs)(whole samples collected without dilution). Water samples collected from May to June 2010 were used for screening tests, with OWD samples slightly more acutely toxic than WAFs. Water samples collected in July through December 2010 were subjected to definitive acute testing with both species. In A. bahia tests, total PAH concentrations for OWD exposures ranged from non-detect to 23.0 μgL^{-1}, while WAF exposures ranged from non-detect to 1.88 μgL^{-1}. Mortality was > 20% in five OWD exposures with A. bahia and three of the WAF definitive tests. Total PAH concentrations were lower for M. beryllina tests, ranging from non-detect to 0.64 μgL-1 and non-detect to 0.17 μgL^{-1} for OWD and WAF exposures, respectively. Only tests from two water samples in both the WAFs and OWDs exhibited >20% mortality to M. beryllina. Microtox assays showed stimulatory and inhibitory responses with no relationship with PAH exposure concentrations. Most mortality in A. bahia and M. beryllina occurred in water samples collected before the well was capped in July 2010 with a clear decline in mortality associated with a decline in total PAH water concentrations.

Echols, B.S., Smith, A.J., Gardinali, P.R., Rand, G.M., The use of ephyrae of a scyphozoan jellyfish, *Aurelia aurita*, in the aquatic toxicological assessment of Macondo oils from the Deepwater Horizon incident, *Chemosphere*, 144, pp. 1893-1900, 2016

Ephyrae of the scyphozoan jellyfish, Aurelia aurita, were evaluated in 96-hr acute toxicity tests for lethal response to Macondo crude oils from the Deepwater Horizon (DWH) incident in the Gulf of Mexico (GOM), Corexit 9500, and oil-dispersant mixtures. Water accommodated fractions (WAFs) of weathered and unweathered Macondo crude oils were not acutely toxic to ephyrae (LC_{50}s > 100% WAF).

The total PAHs (TPAHs), measured as the sum of 46 PAHs, averaged 21.1 and 152 μg TPAH/L for WAFs of weathered and unweathered oil, respectively. Mortality was significantly higher in the three highest exposure concentrations (184-736 μg TPAH/L) of chemically dispersed WAFs (CEWAF) compared to controls. Dispersant only tests resulted in a mean LC_{50} of 32.3 μL/L, which is in the range of previously published LC_{50}s for marine zooplankton. Changes in appearance and muscle contractions were observed in organisms exposed to CEWAF dilutions of 12.5 and 25%, as early as 24 h post-exposure. Based on the results of these tests, crude oil alone did not cause significant acute toxicity; however, the presence of chemical dispersant resulted in substantial mortality and physical and behavioral abnormalities either due to an increase in hydrocarbons or droplet exposure.

Elarbaoui, S., Richard, M., Boufahja, F., Mahmoudi, E., Thomas-Guyon, H., Effect of crude oil exposure and dispersant application on meiofauna: An intertidal mesocosm experiment, *Environmental Sciences: Processes and Impacts*, 17, 5, pp. 997-1004, 2015

The effects of the use of chemical dispersants on meiobenthic organisms and nematodes were investigated in a mesocosm experiment. A 20-day experiment was performed in four experimental sets of mesocosms. In three of them, sediments were contaminated, respectively by oil (500 mg kg^{-1}), dispersed oil (oil + 5% dispersant), and dispersant alone, whereas in the last set sediments were kept undisturbed and used as a reference. The results showed that the meiobenthic response to oil contamination was rapid, for copepods and nematodes. One-way ANOVA showed a significant decrease of the abundance of copepods. In the case of nematodes, univariate and multivariate analyses indicated a clear decrease of the abundance of the species after only 20 days of pollutant exposure. In contrast, Sphaerolaimus gracilis and Sabateria sp. became more frequent within disturbed assemblages and appeared to be resistant and/or opportunistic species in the presence of these kinds of toxicants. Moreover, responses of copepods and nematodes to the treatment seemed to be the same irrespective of whether only oil or oil + dispersant was performed. The main toxicities of dispersed oil appear to be a result of increased quantities of increased dispersed oil droplets.

Esbaugh, A.J., Mager, E.M., Stieglitz, J.D., Hoenig, R., Brown, T.L., French, B.L., Linbo, T.L., Lay, C., Forth, H., Scholz, N.L., Incardona, J.P., Morris, J.M., Benetti, D.D., Grosell, M., The effects of weathering and chemical dispersion on Deepwater Horizon crude oil toxicity to mahi-mahi (Coryphaena hippurus) early life stages, *Science of the Total Environment*, 543, pp. 644-651, 2016

Esbaugh et al. (2016) developed a mahi-mahi spawning program was developed to assess the effect of embryonic exposure to DWH crude oil with particular emphasis on the effects of weathering and dispersant on the magnitude of toxicity. Acute lethality (96 h LC_{50}) ranged from 45.8 μg/L ∑PAH for wellhead oil to 8.8 μg/L ∑PAH for samples collected from the surface slick, reinforcing previous work that weathered oil is more toxic on a ∑PAH basis. Differences in toxicity appear related to the amount of dissolved 3 ringed PAHs. The dispersant Corexit 9500 did not influence acute lethality of oil preparations. Embryonic oil exposure resulted in cardiotoxicity after 48 h, as evident from pericardial edema and reduced atrial contractility. Whereas pericardial edema appeared to correlate well with acute lethality at 96 h, atrial contractility did not. However, sub-lethal cardiotoxicity may impact long-term performance and survival. Dispersant did not affect the occurrence of pericardial edema; however, there was an apparent reduction in atrial contractility at 48 h of exposure. Pericardial edema at 48 h and lethality at 96 h were equally sensitive endpoints in mahi-mahi.

Etnoyer, P.J., Wickes, L.N., Silva, M., Dubick, J.D., Balthis, L., Salgado, E., MacDonald, I.R., Decline in condition of gorgonian octocorals on mesophotic reefs in the northern Gulf of Mexico: before and after the Deepwater Horizon oil spill, *Coral Reefs*, 35, 1, pp. 77-90, 2016

Hard-bottom 'mesophotic' reefs along the '40-fathom' (73 m) shelf edge in the northern Gulf of Mexico were investigated for potential effects of the Deepwater Horizon (DWH) oil spill from the Macondo well in April 2010. Alabama Alps Reef, Roughtongue Reef, and Yellowtail Reef were near the well, situated 60–88 m below floating oil discharged during the DWH spill for several weeks and subject to dispersant applications. In contrast, Coral Trees Reef and Madison Swanson South Reef were far from the DWH spill site and below the slick for less than a week or not at all, respectively. The reefs were surveyed by ROV in 2010, 2011, and 2014 and compared to similar surveys conducted one and two decades earlier. Large gorgonian octocorals were present at all sites in moderate abundance including Swiftia exserta, Hypnogorgia pendula, Thesea spp., and Placogorgia spp. The gorgonians were assessed for health and condition in a before-after-control-impact (BACI) research design using still images captured from ROV video transects. Injury was modeled as a categorical response to proximity and time using logistic regression. The condition of gorgonians at sites near Macondo well declined significantly post-spill. Before the spill, injury was observed for 4–9 % of large gorgonians. After the spill, injury was observed in 38–50 % of large gorgonians. Odds of injury for sites near Macondo were 10.8 times higher post-spill, but unchanged at far sites. The majority of marked injured colonies in 2011 declined further in condition by 2014. Marked healthy colonies generally remained healthy. Background stresses to corals, including fishing activity, fishing debris, and coral predation, were noted during surveys, but do not appear to account for the decline in condition at study sites near Macondo well.

Eygun, C., Cazes, L., Michel, C., Huet, J.Y., Page-Jones, L., Response to a major oil spill from a blow-out incident: The very full scale exercise LULA, *Society of Petroleum Engineers - 1st SPE African Health, Safety, Security and Environment and Social Responsibility Conference and Exhibition 2014 - Protecting People and the Environment: Getting it Right for the Development of the Oil and Gas Industry in Africa*, pp. 226-240, 2014

TOTAL Group chose its Angolan affiliate TOTAL E&P ANGOLA to organize and run a full-scale exercise, code-named "LULA", with the objective of testing the ability to respond to a major oil spill resulting from a deep-sea blow-out. It included the actual mobilization of a newly developed Subsea Dispersant Injection (SSDI) system from Norway and its deployment in the Angolan deep offshore. The response strategy was tested against a 50 000 bopd blow-out scenario in the Angolan deep offshore (water depth l000m). Subsea response involving a Subsea Dispersant Injection kit, SSDI, (developed under a joint industry project SWRP, and managed by Oil Spill Response Limited (OSRL)), was deployed using a newly-designed and built Light Well Intervention Vessel. Surface response offshore with dispersant spraying operations, containment, recovery and storage of the recovered oil.

Fieldhouse, B., Alsaafin, A., Dave, S., Jung, C., Watson, K., Faragher, R., Results from effectiveness testing of chemical countermeasures and sorbent performance on oil sands products, *39th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 572-607, 2016

Fieldhouse et al. (2016) assessed five classes of spill countermeasure on a range of oil sands products and reference oils using standard performance test methods. Dispersant testing indicates that effectiveness is limited by rheological properties in the same manner as other oils; the high proportion of interfacially active asphaltenes and resins in some oil sands products may further reduce dispersibility, especially as weathering occurs. Surface washing agent tests indicate that effectiveness is reduced for highly weathered dilbit residues relative to the other oil sands and reference oils, attributable to the lower mobility of the bituminous residue compared to other oils that contain a higher proportion of mid-range hydrocarbons. Results from herder testing suggest that slicks of fresh oil sands products contract similarly to other oils, with the slick thickness governed primarily by the rheological properties of the oil. Solidifier testing shows only a small variance due to the oil type, with performance tied primarily to the solidifier product itself.

Fieldhouse, B., Mihailov, A., Moruz, V., Weathering of diluted bitumen and implications to the effectiveness of dispersants, *Proceedings of the 37th AMOP Technical Seminar on Environmental Contamination and Response,* pp. 338-352, 2014

Two diluted bitumen products were artificially weathered by rotary evaporator to prepare samples at four weathering states between fresh, to highly weathered residue. The effectiveness of the dispersant Corexit EC9500A was determined for each of the samples by both the low-energy Swirling Flask Test (SFT) and the high-energy Baffled Flask Test (BFT) at temperatures ranging from 5 to 25 °C. The results showed that dispersants were essentially ineffective at all temperatures in the SFT. while the BFT had a somewhat positive result. The BFT results were correlated to the rheologic properties of the samples to establish a limiting threshold value corresponding to a stable dispersion. Pan evaporation experiments were conducted for one week to estimate the exposure time required to reach the weathered states under study at a range of environmentally relevant temperatures. A plot of the rheologic properties against exposure time provided an estimate of the time window-of-opportunity for effective dispersant use at environmental temperatures in the mixing conditions of the BFT. The rapid depletion of volatile components to leave a heavy residue generally limited the effective use of dispersants on diluted bitumen to less than 12 hours at temperatures below 15 °C.

Fingas, M., (prime – PWS) J. Banta, E. Decola, *Prince William Sound Dispersants Monitoring Protocol: Implementation and Enhancement of SMART (Special Monitoring of Applied Response Technologies)*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, Alaska, 49 p., July, 2016

This is a summary of a proposed new monitoring protocol to monitor dispersant application for effectiveness. Suggestions for improvements by the many parties who carried out monitoring work on the Deepwater Horizon are reviewed and new concepts advanced to address these suggestions. The primary decision point for making dispersant applications on a particular day is proposed to be a simple field test. This field test involves a simple method with four repetitions. The other protocols are suggested to be in three 'levels'. Level 1 is an important level involving visual monitoring from an aircraft over the slick. Photographs of effective and not effective dispersant applications are given as a guide. Instructions and points-to-note for this level are given. Level 2 involves towing instruments through the un-dispersed and dispersed slicks at depths of 2 and 5 m. The tow consists of a LISST-100X particle instrument which has an onboard fluorometer (Turner Cyclops-7) and an Aqua Monitor, which is a towed water sampler. A depth meter provides confirmation of sampling depth. The data from the LISST includes an integrated particle count, similar to a Total Petroleum Hydrocarbon (TPH) measurement, and a Volume Mean Diameter (VMD). It is proposed that an effective dispersion results if the integrated particle count (TPH) measurement is at least 10 times the background value and that the VMD is less than 50 µm over a large part of the sample tow. The output of the fluorometer can give confirmation that the particles are oil or not. Water samples are analyzed in the laboratory for TPH and TPAH to confirm field readings. The results of these readings on a particular day and a new field test in the morning would form the basis for a decision for the day's dispersant application. There is Level 3 which consists of taking water samples for further analysis by two different methods. One is using the Payne sampler which provides a separation between particulate and dissolved material. These two samples are analyzed in the laboratory for TPH and TPAH and specific compounds if so desired. Another sample is taken at 2 m and optionally at 5 m using an Alpha sampler. This sample is split into 3 samples, two 1000 mL samples, one for chemical analysis and the other for laboratory toxicity studies. A third smaller split of about 200 mL is used for onboard

MicroTox assessment. Several alternate laboratory analyses are also summarized. The improvements over the previous protocols include the use of particle measurement as an indicator of effectiveness rather than fluorescence; the inclusion of a field effectiveness test and use of a towed sampling device.

Fingas, M., *A Review of Literature Related to Oil Spill Dispersants 2011-2014,* Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, Alaska, 52 p., August, 2014

Fingas (2014) prepared 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.

Fingas, M.F., *A Review of Literature Related to Oil Spill Dispersants, 1997-2008,* Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, Alaska, 168 p., 2008.

This report is a review of the literature on oil spill dispersants published from 1997 to August, 2008. The report identifies and focusses on recent advances in dispersant effectiveness, toxicity, and biodegradation. Other topics such as application, use, behaviour and fate are also covered. The prime motivation for using dispersants is to reduce the impact of oil on shorelines, thus the application must be successful and effectiveness high. As some oil would come ashore, discussion remains on what effectiveness is required to significantly reduce the shoreline impact. A major issue is the actual effectiveness during spills so that these values can be used in estimates for the future. The second motivation for using dispersants is to reduce the impact on birds and mammals on the water surface. The benefits of using dispersants to reduce impacts on wildlife still remain unknown. The third motivation for using dispersants is to promote the biodegradation of oil in the water column. The effect of dispersants on biodegradation is still a matter of dispute. Some papers state that dispersants inhibit biodegradation others indicate that dispersants have little effect on biodegradation. The most recent papers, however, confirm that inhibition is a matter of the surfactant in the dispersant itself and the factors of environmental conditions. It is clear, on the basis of current literature that the surfactants in some of the current dispersant formulations can inhibit biodegradation. No enhancement of biodegradation was clearly shown in any recent studies. Effectiveness remains a major issue with oil spill dispersants. It is important to recognize that many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water. The most important of these is the composition of the oil, followed closely by sea energy. It is equally important to note that the only thing that is important is effectiveness on real spills at sea. More emphasis might be put on monitoring to provide reliable information for assessment and modeling. The results of the review indicate that dispersant effectiveness continues to be a major issue and is unresolved for Alaska North Slope (ANS) crude oil. Results of laboratory testing yield values ranging from 5 to 35%. Field tests show effectiveness values that are fractions of higher energy lab tests even of the moderate-energy tests. Tank tests show very high results, but testing is still to be conducted according to recommended procedures. The results of dispersant toxicity testing are similar to that found in previous years, namely that dispersants vary in their toxicity to various species, however, dispersant toxicity is less than the toxicity of dispersed oil. Of the recent toxicity studies of dispersed oil, most researchers found that chemically-dispersed oil was more toxic than physically-dispersed oil. About half of these found that the cause for this was the increased PAHs, typically about 5 to 10 times, in the water column. Others noted the increased amount of total oil in the water column. Some noted the damage to fish gills caused by the increased amount of droplets. 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. It appears that high concentrations of sediment will have significant effect on dispersed oil droplets and the formation of stable OMAs (Oil-Mineral-Aggregates). OMAs appear to be stable over time and sink slowly and sediment on the bottom. Oil spill dispersions themselves are not stable and dispersed oil will de-stabilize and rise to the surface. Half-lives of dispersions may be between 4 to 24 hours. During the time period covered by this review, the U.S. National Academy of Sciences published a review of dispersants. This report is summarized here and contains many useful insights, summaries and recommendations.

Fingas, M.F., *A Review of Literature Related to Oil Spill Dispersants Especially Relevant to Alaska*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, Alaska, 48 p., 2002.

This is a review of the literature on oil spill dispersants published from 1997 to January, 2002. As in the literature before this time period, it was found that results are often contradictory from one study to another. The paper also identifies and summarizes recent advances in dispersant effectiveness, toxicity, and application technology. The results of the review indicate that dispersant effectiveness continues to be a major issue and is unresolved for Alaska North Slope (ANS) crude oil. Results of one recent dispersant effectiveness study for moderate-energy apparatus demonstrate dispersant effectiveness values ranging from 5 to 15% for ANS crude oil. This study was conducted at water salinities and temperatures known to occur in Alaskan waters, specifically Prince William Sound. High-energy tests such as the MNS, IFP, and EXDET demonstrate higher dispersant effectiveness results, however, the temperatures and salinities used are outside the range of those known for Prince William Sound. New studies question the high values of such tests. Large-scale testing and field tests show effectiveness values that are fractions even of the moderate-energy tests. Since 1997, there have been numerous studies on the toxicity of oil and dispersed oil. Many of these indicated that the acute toxicity of chemically dispersed oil and physically (naturally) dispersed oil is different for different marine test species. In most of the cases, the chemically dispersed oil is somewhat more toxic than the physically dispersed oil. Studies of the food chain indicate that dispersed oil is more likely to result in the passing of naphthalene through the food chain. Similarly, body burdens of PAHs vary depending on the marine species and whether the oil is naturally or chemically dispersed. There is little new in operational matters regarding application of dispersants. The finding that Corexit 9500 is much less effective on thick oil slicks when applied diluted with water than when applied neat is, however, significant. A review of legislation shows that there are no significant changes in dispersant use policy in North America or Europe. There are only eight documented cases of dispersant use in the literature during this time period. One of these is in Nigerian waters, one in Australia, one in Israel, one in Venezuela, one in Britain, and the other three are in the U.S.

Fingas, M., Oil spills and response, *Springer Handbook of Ocean Engineering,* 1067-1093, 2016

This is a general review of oil spills and their cleanup including use of dispersants. Oil spills are random phenomenon and occur in many sizes and forms. The largest 50 spill events are listed, noting that the Gulf War spill in 1991 remains the world's largest oil spill. Organized and rapid response to oil spills is very important to minimize environmental damage. Contingency plans detail the planned response. Five types of oils and fuels are frequently spilled and include gasoline, diesel fuel, light and heavy crude oils, and bunker fuels. Two important properties of these oils include the viscosity and density. The viscosity of spilled products can vary over orders-of- magnitude. The behavior of oils when spilled dictates the environmental impact these will have. The most important oil behaviors are evaporation and water uptake. Evaporation is an exponential factor with time and thus most of the evaporation (about 80%) occurs in the first 2 days. Water uptake takes place in any of the five ways: • Soluble water • Entrained water • Meso-stable emulsions • Stable emulsions • Those that do not form any of the other types or unstable. An important facet of oil spill assessment is laboratory analysis. The most common analytical method is by gas chromatography with mass spectrometric detection (GC-MS) or with flame ionization detection (FID). These methods are not only used for quantification but also for identification and measurement of amounts evaporated or biodegraded. Remote-sensing techniques especially that of satellite radar, are used to map oil spills on the sea. Once spilled, oils on the sea are typically contained using booms and recovered using skimmers, the most important of which are weir and oleophilic surface skimmers. Dealing with recovered oil and disposing of it are important steps. Spill-treating agents are occasionally used, especially oil spill dispersants. There are many conditions and considerations for the use of these. In-situ burning of oil is now being used more frequently and under correct conditions, can rapidly remove spilled oil. Finally, spilled oil often contacts shorelines, therefore assessment and careful removal techniques for shorelines are essential.

Fingas, M., DeepWater Horizon Well Blowout Mass Balance, in *Proceedings of the Fortieth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, in press, 2017a

Fingas (2017a) reviewed the mass balance from the DWH spill. Since an early study on mass balance, much new information has come forward on oil weathering, fates in the sea, skimming and oil on the shoreline. This re-evaluation focusses on the amounts that are readily measured or estimated. The methodology used in this paper was to use literature values or estimation where necessary. The amount of oil released by the blowout was estimated to be 578,000 m^3 (3,635,000 barrels). The amount of oil surfaced is estimated to be about 50% of the oil released. On the surface, skimming removed an estimated 34%, the amount on shore accounted for 19%, burning removed 15%, and weathering accounted for an amount of 11%. The amount of sunken oil and that deposited as marine snow was estimated to be 7%. Oil that moved out of the area was estimated to be 3% and various other fates accounted for 3%. The fate of

6% of the oil is unknown. In the subsurface, fate of the oil was estimated to be dominated by dissolution, 28%, and dispersion in and out of plumes, 18% for each. Marine snow and sedimentation accounted for another 13%, while the fate of about 24% of the oil was unknown. The largest amount of error in this study, is in the estimation of the fate of the subsea oil. On the surface, the amount of oiled shoreline has the largest estimation variances. The remaining variances are generally within 10% of the individual component. A time analysis of the oil on the surface compared to the estimations carried out in this study and compared to remote sensing measurements shows agreement. This comparison shows that the major influences on the amounts of surface oil were the skimming, shoreline encounter and burning. Further influences were the necessary mobilization times, the siphoning of oil from the well over a period of 10 days, Hurricane Alex and the incumbent demobilization of equipment from the sea.

Fingas, M., Development of a Model of Chemical Oil Spill Dispersion, *Proceedings of the Fortieth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, in press, 2017b

Fingas (2017b) described a new model of oil spill dispersion. A model was constructed utilizing four basic processes. Initial dispersion was calculated using the Delvigne equation adjusted to chemical dispersion, then the dispersion was distributed over the mixing depth, as predicted by the wave height. Then the droplets rise to the surface according to Stokes' law. Oil on the surface, from the rising oil and that undispersed, is re-dispersed. The droplets in the water column are subject to coalescence as governed by the Smoluchowski equation. A loss or portion of the amount dispersed, is input to account for the production of small droplets that rise slowly and are not re-integrated with the main surface slick. This is the amount taken as 'permanently' dispersed. More than 1000 runs were carried out with variations of the models. The runs show that the most important factor to the time to extinction of the surface slick, is the mixing depth of the sea as predicted from wind speed. The second most important factor is the viscosity of the starting oil. The model predicts the maximum viscosity that would be dispersed given wind and wave conditions. Variations of the model were developed to enable inputs of only wind speed and oil viscosity. A simplified prediction model was created using regression. The model outputs illustrate the time history of oil-in-water emulsions and the various influences on this time history. The long-term fate of the oil is not modeled.

Fiorello, C.V., Freeman, K., Elias, B.A., Whitmer, E., Ziccardi, M.H., Ophthalmic effects of petroleum dispersant exposure on common murres (Uria aalge): An experimental study, *Marine Pollution Bulletin*, 113, 02-Jan, pp. 387-391, 2016

The group captured common murres and exposed them to Corexit EC9500a, crude oil, or a combination in artificial seawater. they performed ophthalmic examinations and measured intraocular pressures and tear production before and after exposure. They found that exposure to oil or dispersant was related to the development of conjunctivitis and corneal ulcers. Odds ratios for birds exposed to oil or dispersant were positive and significant for the development of conjunctivitis, while odds ratios for the development of corneal ulcers were positive and significant only for birds exposed to a high concentration of oil. Ocular exposure to dispersants and petroleum in seabirds may cause conjunctivitis and may play a role in the development of corneal ulcers.

Fisher, C.R., Demopoulos, A.W.J., Cordes, E.E., Baums, I.B., White, H.K., Bourque, J.R., Coral communities as indicators of ecosystem-level impacts of the Deepwater horizon spill, *BioScience,* 64, 9, pp. 796-07, 2014

Fisher et al. (2014) note that the Macondo oil spill released massive quantities of oil and gas from a depth of 1500 meters. Although a buoyant plume carried released hydrocarbons to the sea surface, as much as half stayed in the water column and much of that in the deep sea. After the hydrocarbons reached the surface, weathering processes, burning, and the use of a dispersant caused hydrocarbon-rich marine snow to sink into the deep sea. As a result, this spill had a greater potential to affect deep-sea communities than had any previous spill. Here, we review the literature on impacts on deep-sea communities from the Macondo blowout and provide additional data on sediment hydrocarbon loads and the impacts on sediment infauna in areas with coral communities around the Macondo well. We review the literature on the genetic connectivity of deep-sea species in the Gulf of Mexico and discuss the potential for wider effects on deep Gulf coral communities.

Fisher, C.R., Montagna, P.A., Sutton, T.T., How did the Deepwater Horizon oil spill impact deep-sea ecosystems? *Oceanography,* 29, 3, pp. 182-195, 2016

These articles review Natural Resource Damage Assessment studies and follow-up work funded as part of the Gulf of Mexico Research Initiative that targeted deep water pelagic and benthic fauna. Oil was incorporated into the pelagic food web, and a reduction in planktonic grazers led to phytoplankton blooms. Fish larvae were killed, and a generation may have been lost. Cetaceans were killed, and many avoided the area of the spill. In the benthic realm, there was a large loss of diversity of soft-bottom infauna, which were still not recovering a year after the DWH oil spill. Colonial octocorals that are anchored to the hard seafloor and are especially vulnerable to anthropogenic impact, died as a result of being covered with flocculent material containing oil and dispersant. Soft- and hard-bottom effects of the oil spill were found as much as 14 km away from the DWH wellhead site. Deep-sea communities in the Gulf of Mexico are diverse, play critical roles in the food web and carbon cycling, affect productivity, are sensitive to perturbations, and are at risk to contaminant exposure

Forth, H.P., Mitchelmore, C.L., Morris, J.M., Lipton, J., Characterization of oil and water accommodated fractions used to conduct aquatic toxicity testing in support of the Deepwater Horizon oil spill natural resource damage assessment, *Environmental Toxicology and Chemistry,* in press, 2016

The authors report on the creation of 4 Deepwater Horizon oils, which encompassed a range of weathering states, and 3 different oil-in-water mixing methods, for a total of 12 unique water accommodated fractions (WAFs). The present study reports on the chemical characteristics of these 4 Deepwater Horizon oils and 12 WAFs. In addition, to better understand exposure chemistry, an examination was conducted of the effects of WAF preparation parameters-including mixing energy, starting oil composition, and oil-to-water mixing ratios-on the chemical profiles and final concentrations of these 12 WAFs. The results showed that the more weathered the starting oil, the lower the concentrations of the oil constituents in the WAF, with a shift in composition to the less soluble compounds. In addition, higher mixing energies increased the presence of insoluble oil constituents. Finally, at low to mid oil-to-water mixing ratios, the concentration and composition of the WAFs changed with changing mixing ratios; this change was not observed at higher mixing ratios (i.e., >1g oil/L).

Frantzen, M., Hansen, B.H., Geraudie, P., Palerud, J., Falk-Petersen, I.-B., Olsen, G.H., Camus, L., Acute and long-term biological effects of mechanically and chemically dispersed oil on lumpsucker (Cyclopterus lumpus), *Marine Environmental Research*, 105, pp. 8-19, 2015

Concentration dependent differences in acute and long-term effects of a 48-h exposure to mechanically or chemically dispersed crude oil were assessed on juvenile lumpsucker (Cyclopterus lumpus). Acute or post-exposure mortality was only observed at oil concentrations representing higher concentrations than reported after real oil spills. Acute mortality was more apparent in chemically than mechanically dispersed oil treatments whereas comparable EC_{50}s were observed for narcosis. There was a positive correlation between EROD activity and muscle PAH concentration for the lower oil concentrations whereas higher concentrations inhibited the enzyme activity. The incidence of gill tissue lesions was low with no difference between dispersion methods or oil concentrations. A concentration dependent decrease in swimming- and feeding behavior and in SGR was observed at the start of the post-exposure period, but with no differences between corresponding oil treatments. Three weeks post-exposure, fish from all treatments showed as high SGR as the control fish.

Frantzen, M., Regoli, F., Ambrose, W.G., Nahrgang, J., Geraudie, P., Benedetti, M., Locke, V W.L., Camus, L., Biological effects of mechanically and chemically dispersed oil on the Icelandic scallop (Chlamys islandica), *Ecotoxicology and Environmental Safety,* 127, pp. 95-107, 2016

Concentration dependent differences in acute responses and long-term effects of a 48-h acute exposure to dispersed oil, with and without the application of a chemical dispersant, were assessed on the Arctic filter feeding bivalve Chlamys islandica. Icelandic scallops were exposed for 48 h to a range of spiked concentrations of mechanically and chemically dispersed oil. Short-term effects were assessed in terms of lysosomal membrane stability, superoxide dismutase, catalase, gluthatione S-transferases, glutathione peroxidases, glutathione reductase, glutathione, total oxyradical scavenging capacity, lipid peroxidation and peroxisomal proliferation. Post-exposure survival, growth and reproductive investment were followed for 2 months to evaluate any long-term consequence. Generally, similar effects were observed in scallops exposed to mechanically and chemically dispersed oil. Limited short-term effects were observed after 48 h, suggesting that a different timing would be required for measuring the possible onset of such effects. There was a concentration dependent increase in cumulative post-exposure mortality, but long-term effects on gonadosomatic index, somatic growth/condition factor did not differ among treatments.

Fraser, G.S., Racine, V., An evaluation of oil spill responses for offshore oil production projects in Newfoundland and Labrador, Canada: Implications for seabird conservation, *Marine Pollution Bulletin,* 107, 1, pp. 36-45, 2016

Fraser and Racine (2016) investigated the response of small spills (<7.95 m^3) at offshore production platforms in Newfoundland, a region recognized for seabird diversity and abundance. In three environmental assessments for oil production operations, Environment Canada requested monitoring and mitigation of small spills potentially impacting seabird populations; suggestions supported by two independent reviews. An industry spill response plan states that operators would collect systematic observations on spills and deploy countermeasures where possible. Operators' spill reports were obtained under an Access to Information request. There were 220 daytime spills with sheens (out of 381 spills; 1997-2010). Of these, six reported time to oil dispersion and eleven the presence or absence of seabirds. Industry self-reporting has not permitted an evaluation of the impact of chronic oil spills on seabirds. Fraser and Racine recommend that independent observers be placed on platforms to systematically collect data on spills and seabirds.

Freitas, B.G., Brito, J.G.M., Brasileiro, P.P.F., Rufino, R.D., Luna, J.M., Santos, V.A., Sarubbo, L.A., Formulation of a commercial biosurfactant for application as a dispersant of petroleum and by-products spilled in oceans, *Frontiers in Microbiology,* 7, OCT, pp,.1646-1652, 2016

Freitas et al. (2016) formulated a biodegradable biosurfactant for application as a dispersant. A biosurfactant was produced by the yeast Candida bombicola URM 3718 cultivated in industrial waste and formulated with the addition of a potassium sorbate preservative for fractionated sterilization and the combination of fluent vaporization with the preservative. After formulation, samples were stored for 120 days, followed by surface tension, emulsification and oil dispersant tests in sea water. The results were promising for the biosurfactant formulated with the preservative, which demonstrated stability. The commercial biosurfactant was tested at different pH values, temperatures and in the presence of salt, demonstrating potential industrial application at a cost compatible with the environmental field.

Friberg, S.E., Hasinovic, H., Belobrov, P., Some Colloidal Fundamentals in Oil Spill Remediation: The Water/Surfactant/Hydrocarbon Combination, *Oil Spill Remediation: Colloid Chemistry-Based Principles and Solutions*, pp. 259-278, 2014

This paper summarizes the basic physical-chemical processes of emulsions relevant to dispersants. The lowest fundamentals are covered including emulsion definitions, processes and phase diagrams.

Fu, J., Cai, Z., Gong, Y., O'Reilly, S.E., Hao, X., Zhao, D., A new technique for determining critical micelle concentrations of surfactants and oil dispersants via UV absorbance of pyrene, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 484, pp. 1-8, 2015

The conventional UV-based methods for determining the critical micelle concentration (CMC) of surfactants often fail for low-solubility surfactants or mixtures of surfactants/solvents or oil dispersants due to baseline uncertainty of the UV spectra. To overcome the limitations, Fu et al. (2015) proposed and tested a new UV-based approach and found that the surfactant concentration, at which the incipient red shift of the strongest UV absorbance peak of pyrene occurs, can be used to roughly locate the range of the CMC for the surfactant. They developed a method, which can accurately pinpoint the CMC graphically by following the change of the maximum measurable peak difference (i.e., the strongest UV absorbance peak minus a weaker reference peak) as a function of the surfactant concentration. Regardless of the baseline fluctuations, the method was able to accurately determine CMCs of 8 model surfactants and oil dispersants. Based on the UV-absorbance analysis, the ratio of pyrene to surfactant molecules in micelles was estimated, which further reveals the roles and abilities of various surfactants in dissolution/dispersion of pyrene or other PAHs in water. The new method can be used to measure CMCs of a wide range of surfactants and oil dispersants.

Fu, J., Gong, Y., Cai, Z., O'Reilly, S.E., Zhao, D., Mechanistic investigation into sunlight-facilitated photodegradation of pyrene in seawater with oil dispersants, *Marine Pollution Bulletin*, 114, 2, pp. 751-758, 2017

These researchers studied the effects of 3 oil dispersants (Corexit EC9500A, Corexit EC9527A and SPC 1000) on photodegradation of pyrene under simulated sunlight. Both Corexit dispersants enhanced photodegradation of pyrene, while SPC1000 slightly inhibited the reaction. Span 80 and Tween 85 were the key ingredients causing the effects, though the underlying mechanisms differed. Span 80 enriches pyrene in the upper layer of water column, whereas Tween 85 induces a photosensitization process. Two reactive oxygen species, $^1O_2$ and O_2[rad]−, were found responsible for pyrene photodegradation, though the presence of EC9500A suppressed the $^1O_2$ pathway. In terms of photodegradation products, EC9500A enhanced generation of polyaromatic intermediates, i.e., phenaleno[1,9-cd][1,2]dioxine, 1-hydroxypyrene, and 1,8-pyrenequinone, but did not alter the classical photodegradation pathway. The Corexit dispersants were more prone to photochemical decomposition, with multiple by-products detected.

García-Olivares, A., García-Ladona, E., Jiménez Madrid, J.A., Management of large oil spills, *Marine Pollution: Types, Environmental Significance and Management Strategies*, pp. 55-111, 2014

This book chapter reviews major spills which produce major ecological and economic impacts on shorelines depending on the following conditions: (i) persistence of the oil in the environment; (ii) weather and sea conditions; (iii) amount and rate of spillage; (iv) geographical, biological and economic characteristics of the area affected; (v) effectiveness of clean up. Oil spill dispersion models are necessary tools to forecast the trajectory and persistence of oil slicks following a marine accident. However, their reliability depends on the quality of available meteorological and hydrological data and assimilation strategies. Large oil spills that took place in regions relatively distant from the coast, such as the Prestige accident in November 2002 and the DeepWater Horizon explosion in April 2010, showed the need for having both a short-term forecast for the days following the accident as well as a long-term forecast to prevent future pollution impact. However, there is still no universally accepted methodology for the management of this kind of oil spill. A combined forecast of the short-term deterministic trajectory and the long-term probabilistic dispersion of the slicks may be useful to delimit the most probable consequences of any spill. Medess-4MS is an example of an integrated operational multi-model oil spill system which is under development to meet both requirements. This double methodology is illustrated by the analysis of the oil spill produced by the supertanker Prestige near the Spanish coast in November 2002. This double forecast makes it possible to obtain the short-term and long-term probability of oil beaching on different shoreline segments, followed by preliminary estimates of ecological risk, and economic cost based on the analysis of past similar accidents.

Girard, F., Fu, B., Fisher, C.R., Mutualistic symbiosis with ophiuroids limited the impact of the Deepwater Horizon oil spill on deep-sea octocorals, *Marine Ecology Progress Series*, 549, pp. 89-98, 2016

The researchers focused on the influence of the ophiuroid symbiont Asteroschema clavigerum on the resilience of its octocoral host Paramuricea biscaya after the Deepwater Horizon oil spill in the Gulf of Mexico. Corals were imaged between 2011 and 2014 at 4 sites, 3 of which were impacted by the spill. Each colony was digitized to quantify the impact on corals. They developed a method to define an area under the influence of ophiuroids for each coral colony. The level of total visible impact, as well as recovery, was then compared within and outside this area. For the majority of colonies, recovery from visible impact and hydroid colonization was negatively correlated with distance from the ophiuroid. Total visible impact was lower within the area influenced by ophiuroids, and branches within this area were more likely to recover. These results indicate that P. biscaya benefits from its association with A. clavigerum, likely through the physical action of ophiuroids removing material depositing on polyps, and perhaps inhibiting the settlement of hydroids.

Glover, C.M., Mezyk, S.P., Linden, K.G., Rosario-Ortiz, F.L., Photochemical degradation of Corexit components in ocean water, *Chemosphere*, 111, pp. 596-602, 2014

Direct and sensitized photolysis experiments were carried out for two compounds chosen as surrogates for the Corexit mixture (9500 and 9527) that were applied to surface waters during the oil spill in the Gulf of Mexico. The results showed that direct photolysis did not contribute significantly to the overall degradation (max ~30%), therefore the focus shifted to sensitized photolysis, specifically the degradation stemming from the reaction rate with hydroxyl radical ($HO^{\cdot}$). The direct photochemical degradation rates for two of the compounds, dioctyl sulfosuccinate (DOSS) and dipropylene glycol butyl ether (DGBE) were measured as $4.29\times10^{-6}s^{-1}$ and $5.95\times10^{-6}s^{-1}$, respectively; whereas the overall degradation rate in ocean water was $1.56\times10^{-5}s^{-1}$ and $2.23\times10^{-5}s^{-1}$. The formation rates and apparent quantum yields for $HO^{\cdot}$ formation were determined for six ocean water samples. The values ranged from 1.81×10^{-5} near shore to 0.061×10^{-5} for the open ocean. These degradation rates suggest the possibility for photolysis to play a role in the overall fate of Corexit if the product resides near the surface.

Gong, H., Bao, M., Pi, G., Li, Y., Wang, A., Wang, Z., Dodecanol-Modified Petroleum Hydrocarbon Degrading Bacteria for Oil Spill Remediation: Double Effect on Dispersion and Degradation, *ACS Sustainable Chemistry and Engineering,* 4, 1, pp. 169-176, 2016

The researchers modified petroleum hydrocarbon degrading bacteria, Bacillus cereus S-1, with dodecanol to produce an oil-in-water (o/w) Pickering emulsion. In a set concentration range, the presence of dodecanol improved the surface hydrophobicity and wettability of bacterial cells, which was responsible for their adsorption at the oil-water interface. When a sufficient amount of bacteria was added, only a small amount of dodecanol was required to obtain stable emulsions. However, stable emulsion was not prepared with unmodified Bacillus cereus S-1 cells. Scanning electron microscopy (SEM) and confocal laser scanning microscope (CLSM) images indicated that the effective emulsification was attributed to the formation of a dense bacterial interfacial film around oil drops, providing a steric barrier to impeding droplet coalescence.

Gong, H., Li, Y., Bao, M., Lv, D., Wang, Z., Petroleum hydrocarbon degrading bacteria associated with chitosan as effective particle-stabilizers for oil emulsification, *RSC Advances*, 5, 47, pp. 37640-37647, 2015

Gong et al. (2015) investigated oil-in-water emulsions stabilized by self-assembled complexes of the hydrocarbon degrading bacteria, Bacillus cereus S-1, with the polysaccharide chitosan. They found that the addition of chitosan improves the ability of hydrophilic Bacillus cereus S-1 to function as an effective emulsifier. The self-assembled complex of Bacillus cereus S-1 and chitosan was able to adsorb on the interface and stabilize oil-in-water emulsions for months. Confocal laser scanning microscope (CLSM) imaging and SEM results showed that the oil-in-water emulsions were stable against coalescence by formation of a thin film of the bacteria-chitosan complex. Bacillus cereus S-1 associated with chitosan in the aqueous phase gave rise to a network, which was also responsible for the emulsion stability. The bacteria were still able to degrade oil.

Gong, Y., Zhao, D., Effects of oil dispersant on ozone oxidation of phenanthrene and pyrene in marine water, *Chemosphere*, 172, pp. 468-475, 2017

Gong and Zhao (2017) investigated effects of Corexit EC9500A on the oxidation of phenanthrene and pyrene (two model polycyclic aromatic hydrocarbons) in Gulf coast seawater under simulated atmospheric ozone. The degradation data followed a two-stage pseudo-first order kinetics, a slower initial reaction rate followed by a much faster rate in longer time. The ozonation rate for pyrene was faster than that for phenanthrene. The presence of 18 and 180 mg/L of the dispersant inhibited the first-order degradation rate by 32–80% for phenanthrene, and 51–85% for pyrene. In the presence of 18 mg/L of the dispersant, the pyrene degradation rate increased with increasing ozone concentration, but decreased with increasing solution pH and temperature, while remaining independent of ionic strength.

Goodman, R., Oil spill mass balance: Is it a myth? *Proceedings of the 37th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 90-93, 2014

This paper discusses the potential of measuring mass balance for dispersant experiments, especially related to those in tanks. The difficulty is that of measuring the thickness. Discussions centre around this facet of the issue.

Green, L.C., Lester, R.R., Zemba, S.G., Evaluation of exposure to airborne contaminants during the Deepwater horizon oil spill, *Proceedings of the Air and Waste Management Association's Annual Conference and Exhibition, AWMA*, 4, pp. 2926-2935, 2014

A 5-yr study was designed to identify potential long-term health effects to workers involved in the response to the Deepwater Horizon Oil spill. The levels of contaminant exposure received by Deepwater Horizon response workers were evaluated and the aspects of exposure were compared to the limited amount of information available for the Prestige oil spill response for which researchers have reported evidence of long-term health effects. Monitored chemicals included: various measures of oil and its constituents (e.g., petroleum distillates, BTEX compounds, and H_2S), the dispersants employed to break up the oil (e.g., 2-butoxyethanol), and combustion by-products (e.g., PAH). The frequencies and concentrations of chemicals detected in air were reviewed; and using benzene as an example, evaluated to determine whether exposures led to adverse acute and chronic effects on human health. Approximately 89% of the measurements for Deepwater Horizon cleanup workers were less than measurements reported for paid cleanup workers during the Prestige spill, largely the result of the differing nature of the two releases.

Gros, J., Nabi, D., Würz, B., Wick, L.Y., Brussaard, C.P.D., Huisman, J., Van Der Meer, J.R., Reddy, C.M., Arey, J.S., First day of an oil spill on the open sea: Early mass transfers of hydrocarbons to air and water, *Environmental Science and Technology*, 48, 16, pp. 9400-9411, 2014

This paper discusses the rapid partition of hydrocarbons during the first hours after release of petroleum at sea. Limited information is available about very early evaporation and dissolution processes. The authors report on the composition of the oil slick during the first day after a permitted, unrestrained 4.3 m^3 oil release conducted on the North Sea. Rapid mass transfers of volatile and soluble hydrocarbons were observed, with >50% of ≤C17 hydrocarbons disappearing within 25 h from this oil slick of <10 km^2 area and <10 μm thickness. For oil sheens, >50% losses of ≤C16 hydrocarbons were observed after 1 h. They developed a mass transfer model to describe the evolution of oil slick chemical composition and water column hydrocarbon concentrations. The model was parametrized based on environmental conditions and hydrocarbon partitioning properties estimated from comprehensive two-dimensional gas chromatography (GC×GC) retention data. The model correctly predicted the observed fractionation of petroleum hydrocarbons in the oil slick resulting from evaporation and dissolution.

Guo, W., Hao, Y., Zhang, L., Xu, T., Ren, X., Cao, F., Wang, S., Development and application of an oil spill model with wave-current interactions in coastal areas, *Marine Pollution Bulletin*, 84, 02-Jan, pp. 213-224, 2014

Guo et al. (2014) develop a numerical oil spill model that incorporates the full three-dimensional wave-current interactions for representation of the spilled oil transport mechanics in coastal environments. The incorporation of surface wave effects is not only imposing a traditional drag coefficient formulation at the free surface, but also the 3D momentum equations are adjusted to include the impact of the vertically dependent radiation stresses on the currents. Based on the current data from SELFE and wave data from SWAN, the oil spill model utilizes oil particle method to predict the trajectory of individual droplets and the oil concentration.

Gupta, A., Sender, M., Fields, S., Bothun, G.D., Phase and sedimentation behavior of oil (octane) dispersions in the presence of model mineral aggregates, *Marine Pollution Bulletin*, 87, 1 , pp. 164-170, 2014

Gupta et al. discuss adsorption of suspended particles to the interface of surfactant-dispersed oil droplets altering emulsion phase and sedimentation behavior. This work examined the effects of model mineral aggregates (silica nanoparticle aggregates or SNAs) on the behavior of oil (octane)-water emulsions prepared using sodium bis(2-ethylhexyl) sulfosuccinate (DOSS). Experiments were conducted at different SNA hydrophobicities in deionized and synthetic seawater (SSW), and at 0.5. mM and 2.5.

mM DOSS. SNAs were characterized by thermogravimetric analysis (TGA) and dynamic light scattering (DLS), and the emulsions were examined by optical and cryogenic scanning electron microscopy. In deionized water, oil-in-water emulsions were formed with DOSS and the SNAs did not adhere to the droplets or alter emulsion behavior. In SSW, water-in-oil emulsions were formed with DOSS and SNA-DOSS binding through cation-bridging led to phase inversion to oil-in-water emulsions. Droplet oil-mineral aggregates (OMAs) were observed for hydrophilic SNAs, while hydrophobic SNAs yielded quickly- sedimenting agglomerated OMAs.

Gustitus, S.A., John, G.F., Clement, T.P., Effects of weathering on the dispersion of crude oil through oil-mineral aggregation, *Science of the Total Environment*, 587-588, pp. 36-46, 2017

Gustitus et al. (2017) identified two conflicting hypotheses in the literature: OMA formation 1) increases with weathering as a result of increased asphaltene and polar compound content; or 2) decreases with weathering as a result of increased viscosity. While it is indeed true that the viscosity and the relative amounts of polar compounds will increase with weathering, their net effects on OMA formation is unclear. Controlled laboratory experiments were carried out to systematically test these two conflicting hypotheses. Experimental results using light, intermediate, and heavy crude oils, each at five weathering stages, show a decrease in OMA formation as oil weathers, showing that hypothesis 2) is correct.

Hansen, B.H., Altin, D., Nordtug, T., Øverjordet, I.B., Olsen, A.J., Krause, D., Størdal, I., Størseth, T.R., Exposure to crude oil micro-droplets causes reduced food uptake in copepods associated with alteration in their metabolic profiles, *Aquatic Toxicology*, 184, pp. 94-102, 2017

Hansen et al. (2017) studied the contribution of oil micro-droplet toxicity in dispersions by comparing exposures to oil dispersions (water soluble fraction with droplets) to concurrent exposure to filtered dispersions (water-soluble fractions without droplets). Physical (coloration) and behavioral (feeding activity) as well as molecular (metabolite profiling) responses to oil exposures in the copepod Calanus finmarchicus were studied. At high dispersion concentrations (4.1–5.6 mg oil/L), copepods displayed carapace discoloration and reduced swimming activity. Reduced feeding activity, measured as algae uptake, gut filling and fecal pellet production, was evident also for lower concentrations (0.08 mg oil/L). Alterations in metabolic profiles were also observed following exposure to oil dispersions. The pattern of responses was similar between two comparable experiments with different oil types, suggesting responses to be non-oil type specific. Furthermore, oil micro-droplets appear to contribute to some of the observed effects triggering a starvation-type response, manifested as a reduction in metabolite (homarine, acetylcholine, creatine and lactate) concentrations in copepods. The work clearly displays a relationship between crude oil micro-droplet exposure and reduced uptake of algae in copepods.

Hansen, B.H., Salaberria, I., Olsen, A.J., Read, K.E., Øverjordet, I.B., Hammer, K.M., Altin, D., Nordtug, T., Reproduction dynamics in copepods following exposure to chemically and mechanically dispersed crude oil, *Environmental Science and Technology*, 49, 6, pp. 3822-3829, 2015

The researchers studied the potential contribution of dispersants to the reproductive effects of dispersed crude oil in the marine copepod *Calanus finmarchicus* (Gunnerus) was isolated by keeping the oil concentrations and oil droplet size distributions comparable between parallel chemically dispersed (CD, dispersant:oil ratio 1:25) and mechanically dispersed oil (MD, no dispersant) exposures. Female copepods were exposed for 96 h to CD or MD in oil concentration range of 0.2-5.5 mg/L after which they were subjected to a 25-day recovery period where production of eggs and nauplii were compared between treatments. The two highest concentrations, both in the upper range of dispersed oil concentrations reported during spills, caused a lower initial production of eggs/nauplii for both MD and CD exposures. However, copepods exposed to mechanically dispersed oil exhibited compensatory reproduction during the last 10 days of the recovery period, reaching control level of cumulative egg and nauplii production whereas females exposed to a mixture of oil and dispersant did not.

Haule, K., Freda, W., The effect of dispersed Petrobaltic oil droplet size on photosynthetically active radiation in marine environment, *Environmental Science and Pollution Research*, 23, 7, pp. 6506-6516, 2016

Haule and Freda (2016) examined the influence of oil droplet size of highly dispersed Petrobaltic crude on the underwater visible light flux and the inherent optical properties (IOPs) of seawater, including absorption, scattering, backscattering and attenuation coefficients. On the basis of measured data and Mie theory, they calculated the IOPs of dispersed Petrobaltic crude oil in constant concentrations, but different log-normal size distributions. They also performed a radiative transfer analysis, in order to evaluate the influence on the downwelling irradiance E_d, remote sensing reflectance R_{rs} and diffuse reflectance R, using in situ data from the Baltic Sea. They found that during dispersion, there occurs a boundary size distribution characterized by a peak diameter d_0 = 0.3 μm causing a maximum E_d increase of 40 % within 0.5-m depth, and the maximum Ed decrease of 100 % at depths below 5 m. They showed that the impact of size distribution on the "blue to green" ratios of R_{rs} and R varies from 24 % increase to 27 % decrease at the same crude oil concentration.

Hazen, T.C., Prince, R.C., Mahmoudi, N., Marine Oil Biodegradation, *Environmental Science and Technology*, 50, 5, pp. 2121-2129, 2016

The authors review marine oil biodegradation with emphasis on the positive benefits of dispersants. They note that catastrophic oil spills stimulate these biodegradation organisms to bloom in a reproducible fashion, and although oil does not provide bioavailable nitrogen, phosphorus or iron, there are enough of these nutrients in the sea that when dispersed oil droplets dilute to low concentrations these low levels are adequate for microbial growth. Most of the hydrocarbons in dispersed oil are degraded in aerobic marine waters with a half-life of days to months. In contrast, oil that reaches shorelines is likely to be too concentrated, have lower levels of nutrients, and have a far longer residence time in the environment. Oil that becomes entrained in anaerobic sediments is also likely to have a long residence time, although it too will eventually be biodegraded.

Hernandez, F.J., Filbrun, J.E., Fang, J., Ransom, J.T., Condition of larval red snapper (*Lutjanus campechanus*) relative to environmental variability and the Deepwater Horizon oil spill, *Environmental Research Letters*, 11, 9, 94019, 2016

Hernandez et al. (2016) studied the effects of the DeepWater Horizon spill on larval Red Snapper, data from a long-term ichthyoplankton survey off the coast of Alabama examining: (1) larval abundances among pre-impact (2007-2009), impact (2010), and post-impact (2011, 2013) periods; (2) proxies for larval condition (size-adjusted morphometric relationships and dry weight) among the same periods; and (3) the effects of background environmental variation on larval condition. They found that larval Red Snapper were in poorer body condition during 2010, 2011, and 2013 as compared to the 2007-2009 period, a trend that was strongly and negatively related to variation in Mobile Bay freshwater discharge. However, larvae collected during and after 2010 were in relatively poor condition even after accounting for variation in freshwater discharge and other environmental variables. By contrast, no differences in larval abundance were detected during these survey years. Taken together, larval supply did not change relative to the timing of the DWH, but larval condition was negatively impacted. Even small changes in condition can affect larval survival, so these trends may have consequences for recruitment of larvae to juvenile and adult life stages.

Hope, N., Gideon, A., Biosurfactant production from Palm Oil Mill Effluent (POME) for applications as oil field chemical in Nigeria, *Society of Petroleum Engineers - SPE Nigeria Annual International Conference and Exhibition, NAICE 2015*, 2015

The researchers produced a dispersant from Palm Oil Mill Effluent (POME).

Irving, P., Lee, K., Improving Australia's dispersant response strategy, *Proceedings of the 38th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 973-987, 2015

The Australian Maritime Safety Authority (AMSA) has three distinct roles about dispersants: gatekeeper, responder and advisor. AMSA has commissioned independent scientific and research studies to better understand, evaluate and communicate the safety hazards and environmental risks in Australian waters. Ongoing studies are addressing a number of knowledge gaps including health hazards, eco-toxicology and real-time in-situ monitoring. The results from these and future projects will improve dispersant policy, procedure, purchase, use, monitoring and communications.

Jaggi, A., Snowdon, R.W., Stopford, A., Radović, J.R., Oldenburg, T.B.P., Larter, S.R., Experimental simulation of crude oil-water partitioning behavior of BTEX compounds during a deep submarine oil spill, *Organic Geochemistry*, 108, 1-8, 2017

Jaggi et al. (2017) noted that the conventional shake flask technique for determining oil-water partition ratios of benzene, toluene, ethylbenzene and xylene (BTEX) cannot accurately assess the extremes of high pressure and low water temperatures found in submarine oil spill conditions. An oil-water partitioning device has been constructed to experimentally simulate the partition behavior of BTEX compounds under submarine oil spill conditions, using simulated live oil (methane-charged), with saline waters over a range of pressure (2–15 MPa) and temperature (4–20 °C). Within the investigated ranges, the partition ratios of BTEX compounds increase proportionally with an increase in methane charging pressure (oil saturation pressure) and the degree of BTEX alkylation, and decrease with increase in temperature. The variation of the partition ratio values due to changes in system pressure and increasing oil methane concentration, is much more significant than those seen due to change in the temperature over the range studied. This data may be used in near-field and far-field distribution modeling of the environmental fate of highly toxic BTEX compounds, derived from submarine oil spills and their impact on the ecosystem. The parameters will also aid in the prediction of oil migration and dispersion away from the spill thus helping to improve response strategies.

Johansen, T., Reed, M., Bodsberg, N.R., *Natural dispersion revisited*, *Marine Pollution Bulletin*, 93, 02-Jan, pp. 20-26, 2015

This paper presents a new semi-empirical model for oil droplet size distributions generated by single breaking wave events. Empirical data was obtained from laboratory experiments with different crude oils at different stages of weathering. The paper starts with a review of the most commonly used model for natural dispersion, which is followed by a presentation of the laboratory study on oil droplet size distributions formed by breaking waves conducted by SINTEF on behalf of the NOAA/UNH Coastal Response Research Center. The next section presents the theoretical and empirical foundation for the new model. The model is based on dimensional analysis and contains two non-dimensional groups; the Weber and Reynolds number. The model was validated with data from a full scale experimental oil spill conducted in the Haltenbanken area offshore Norway in July 1982.

John, V., Arnosti, C., Field, J., Kujawinski, E., McCormick, A., The role of dispersants in oil spill remediation: Fundamental concepts, rationale for use, fate, and transport issues , *Oceanography*, 29, 3, pp. 108-117, 2016

This paper provides a rationale for the use of dispersants in oil spill remediation by discussing their formulations and modes of action and connecting their physics and chemistry to their environmental fates and impacts. With the first use of dispersants at the source of the oil release during the Deepwater Horizon incident, there is a new great need for understanding the efficiency and the environmental impacts of their use. The paper concludes with some cautionary recommendations on dispersant research.

King, G.M., Kostka, J.E., Hazen, T.C., Sobecky, P.A., Microbial responses to the Deepwater Horizon Oil spill: From Coastal Wetlands to the Deep Sea, *Annual Review of Marine Science*, 7, pp. 377-401, 2015a

The scientists discuss results of bacterial surveys following the DeepWater Horizon Spill which have shown an unexpectedly rapid response of deep-sea Gammaproteobacteria to oil and gas and documented a distinct succession correlated with the control of the oil flow and well shut-in. Similar successional events, also involving Gammaproteobacteria, have been observed in nearshore systems. The scientist note that no connection can be definitively drawn to these events and the use of dispersants.

King, T., Robinson, B., Ryan, S., Lu, Y., Zhou, Q., Ju, L., Li, J., Sun, P., Lee, K., Fate of Chinese and Canadian oils treated with dispersants in a wave tank, *Proceedings of the 38th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 798-811, 2015b

King et al. (2015b) elucidate the dispersion characteristics of three oil products (Canadian Cold Lake diluted bitumen, Chinese medium and heavy crude oils) treated using two chemical dispersant products (Corexit 9500 and a proprietary Chinese dispersant formulation) to provide information for the development of spill response policies and operational guidance documents. Experiments were conducted using breaking wave conditions generated in a wave tank facility located in Atlantic Canada. The Cold Lake diluted bitumen was effectively dispersed by Corexit 9500 under the test conditions in this study. Neither of the two dispersant products effectively dispersed the Chinese oils, especially the medium crude oil. Chemical analysis using gas chromatography/mass spectrometry revealed that the Chinese medium crude contained a greater proportion of n-alkanes (C9-C38) compared to the other oils. This product would be defined as a waxy crude, since it consists mostly of paraffin hydrocarbons (C18-C36) resulting in a high viscosity at low temperature. Since the wax content of crude oil can affect its rheological properties, the medium crude is less likely to spread into a thin film that promotes the dispersibility of the product in coastal waters with temperatures < 16°C.

King, T.L., Robinson, B., McIntyre, C., Toole, P., Ryan, S., Saleh, F., Boufadel, M.C., Lee, K., Fate of surface spills of cold lake blend diluted bitumen treated with dispersant and mineral fines in a wave tank, *Environmental Engineering Science*, 32, 3, pp. 250-261, 2015c

Cold Lake Blend (CLB) used diluted bitumen (Dilbit) to evaluate the fate and transport of pre-weathered (6.2% w/w) Dilbit under environmental conditions both in spring (seawater temperature 8.5°C°C and salinity 27.7 practical salinity units [psu]) and in summer (seawater temperature 17.0°C and salinity 26.8 psu). The following oil spill treatments were considered: no treatment, dispersant alone, mineral fines (MF) alone, and dispersant+MF. The aim was to determine their influences on the fate of spilled CLB at sea. When dispersant alone was used, the highest dispersion effectiveness (DE) was noted, and DE ranged from 45% to 59% under the selected environmental conditions. With no treatment and treatment of MF alone, CLB DE was insufficient under tested conditions. Total petroleum hydrocarbon (TPH) concentration in the water column was highest for the dispersant alone, followed by that of dispersant+MF. TPH concentration for the dispersant alone increased abruptly with time. Droplet size distribution (DSD) resulting from dispersant alone had a unimodal shape, which was different than previously observed when conventional oils were treated with the dispersant. Cases of dispersant+MF were thus characterized by a broader DSD compared with dispersant only and a gradual increase in TPH concentration.

Kinner, N.E., Belden, L., Kinner, P., Unexpected sink for Deepwater horizon oil may influence future spill response, *Town Hall: Marine oil snow Sedimentation and Flocculent Accumulation (MOSSFA); Mobile, Alabama, 27 January 2014*, Eos, 95, 21, p. 176, 2014

This reports on a town hall meeting where fate of DWH oil was discussed. Scientists from different research consortia studying sediments and marine snow in the Gulf began to observe signs of increased sedimentation and hydrocarbon deposition. Sediment mass accumulation rates for the northern Gulf of Mexico increased sixfold to eightfold in 2010, directly following the DWH blowout.

Kirby, S.M., Anna, S.L., Walker, L.M., Sequential adsorption of an irreversibly adsorbed nonionic surfactant and an anionic surfactant at an oil/aqueous interface, *Langmuir*, 31, 14, pp. 4063-4071, 2015

Kirby et al. (2015) study two surfactants, Aerosol-OT (AOT) and Tween 80 which are two of the main surfactants in commercial dispersants used in response to oil spills. Understanding how multicomponent surfactant systems interact at oil/aqueous interfaces is crucial for improving both dispersant design and application efficacy. This is true of many multicomponent formulations; a lack of understanding of competition for the oil/water interface hinders formulation optimization. In this study, they characterized the sequential adsorption behavior of AOT on squalane/aqueous interfaces that have been precoated with Tween 80. A microtensiometer was used to measure the dynamic interfacial tension of the system. Tween 80 either partially or completely irreversibly adsorbs to squalane/aqueous interfaces when rinsed with deionized water. These Tween 80 coated interfaces are then exposed to AOT. AOT adsorption increases with AOT concentration for all Tween 80 coverages, and the resulting steady-state interfacial tension values are interpreted using a Langmuir isotherm model. In the presence of 0.5 M NaCl, AOT adsorption significantly increases due to counterion charge screening of the negatively charged head groups. The presence of Tween 80 on the interface inhibits AOT adsorption, reducing the maximum surface coverage as compared to a clean interface. Tween 80 persists on the interface even after exposure to high concentrations of AOT.

Kleindienst, S., Grim, S., Sogin, M., Bracco, A., Crespo-Medina, M., Joye, S.B., Diverse, rare microbial taxa responded to the Deepwater Horizon deep-sea hydrocarbon plume, *ISME Journal*, 10, 2, pp. 400-415, 2016a

Kleindienst et al. (2016a) observed an enrichment of distinct microbial populations after the DWH spill, yet, little is known about the abundance and richness of specific microbial ecotypes involved in gas, oil and dispersant biodegradation in the wake of oil spills. They document a previously unrecognized diversity of closely related taxa affiliating with Cycloclasticus, Colwellia and Oceanospirillaceae and describe their spatio-temporal distribution in the Gulf's deepwater, in close proximity to the discharge site and at increasing distance from it, before, during and after the discharge. A highly sensitive, computational method (oligotyping) applied to a data set generated from 454-tag pyrosequencing of bacterial 16S ribosomal RNA gene V4-V6 regions, enabled the detection of population dynamics at the sub-operational taxonomic unit level (0.2% sequence similarity). The biogeochemical signature of the deep-sea samples was assessed via total cell counts, concentrations of short-chain alkanes (C1-C 5), nutrients, (colored) dissolved organic and inorganic carbon, as well as methane oxidation rates. Statistical analysis elucidated environmental factors that shaped ecologically relevant dynamics of oligotypes, which likely represent distinct ecotypes. Major hydrocarbon degraders, adapted to the slow-diffusive natural hydrocarbon seepage in the Gulf of Mexico, appeared unable to cope with the conditions encountered during the DWH spill or were outcompeted. In contrast, diverse, rare taxa increased rapidly in abundance, underscoring the importance of specialized sub-populations and potential ecotypes during massive deep-sea oil discharges and perhaps other large-scale perturbations.

Kleindienst, S., Paul, J.H., Joye, S.B., Using dispersants after oil spills: Impacts on the composition and activity of microbial communities, *Nature Reviews Microbiology*, 13, 6, pp. 388-396, 2015

Kleindienst et. al. (2015) publish findings showing that the use of dispersants modifies the composition of the microbial community, often diminishing those of oleoclastic communities. These results are controversial, probably owing to variations in laboratory methods, the selected model organisms and the chemistry of different dispersant-oil mixtures. Here, they argue that an in-depth assessment of the impacts of dispersants on microorganisms is needed to evaluate the planning and use of dispersants during future responses to oil spills.

Kleindienst, S., Seidel, M., Ziervogel, K., Grim, S., Loftis, K., Harrison, S., Malkin, S.Y., Perkins, M.J., Field, J., Sogin, M.L., Dittmar, T., Passow, U., Medeiros P., Joye S.B., Ability of chemical dispersants to reduce oil spill impacts remains unclear, *Proceedings of the National Academy of Sciences of the United States of America*, 113, 11, pp. E1422-E1423, 2016b

This is a reply to a criticism of a study which showed that dispersants slow oil biodegradation.

Kleindienst, S., Seidel, M., Ziervogel, K., Grim, S., Loftis, K., Harrison, S., Malkin, S.Y., Perkins, M.J., Field, J., Sogin, M.L., Dittmar, T., Passow, U., Medeiros, P.M., Joye, S.B., Chemical dispersants can suppress the activity of natural oil-degrading microorganisms, *Proceedings of the National Academy of Sciences of the United States of America*, 112, 48, pp. 14900-14905, 2015c

Kleindienst et al. (2016c) simulated environmental conditions comparable to the hydrocarbon-rich, 1,100 m deep plume that formed during the Deepwater Horizon discharge. The presence of dispersant significantly altered the microbial community composition through selection for potential dispersant-degrading Colwellia, which also bloomed in situ in Gulf deep waters during the discharge. In contrast, oil addition to deepwater samples in the absence of dispersant stimulated growth of natural hydrocarbon-degrading Marinobacter. In these deepwater microcosm experiments, dispersants did not enhance heterotrophic microbial activity or hydrocarbon oxidation rates. An experiment with surface seawater from an anthropogenically derived oil slick corroborated the Deepwater microcosm results as inhibition of hydrocarbon turnover was observed in the presence of dispersants, suggesting that the microcosm findings are broadly applicable across marine habitats. Extrapolating this comprehensive dataset to real world scenarios questions whether dispersants stimulate microbial oil degradation in deep ocean waters and instead highlights that dispersants can exert a negative effect on microbial hydrocarbon degradation rates.

Kuang, C., Xie, H., Su, P., Chen, K., Numerical simulation and analysis of transport and fate of Penglai 19-3 oil spill, Tongji Daxue Xuebao/Journal of Tongji University, 44, 10, pp. 1585-1594, 2016

The authors describe a numerical model of oil spill transport and fate in the Bohai Sea implemented by coupling with the hydrodynamic model. The change processes of spilled oil included in the model are drift, dispersion, evaporation, emulsification and so on. The drift process is simulated by the Lagrange method, while the turbulent dispersion process is considered by using the `Monte Carlo method', turbulent dispersion of spilled oil changes over time by using the time-varying turbulent dispersion coefficient.

Laitinen, O., Ojala, J., Sirviö, J.A., Liimatainen, H., Sustainable stabilization of oil in water emulsions by cellulose nanocrystals synthesized from deep eutectic solvents, *Cellulose*, pp. 1-11, 2017

The authors used cellulose nanocrystals (CNC) which were synthesized using a deep eutectic solvent (DES) and two commercially available cellulose nanocrystals were used as marine diesel oil–water Pickering emulsion stabilizers. In particular, oil in water (o/w) emulsion formation and stability of emulsified oil during storage were addressed using a laser diffraction particle size analyzer, image analysis, and oil emulsion volume examination. The particle size of the o/w reference without CNCs after dispersing was over 50 µm and coalescence occurred only a few minutes after the emulsifying mixing procedure. All three investigated CNCs were effective stabilizers for the o/w system (oil droplets size under 10 µm) by preventing the oil droplet coalescence over time (6 weeks) and resulting in a stable creaming layer. The CNCs prepared using green DES systems boasted performance comparable to that of commercial CNCs, and they showed effectiveness at 0.1% dispersant dosage.

Lambert, R.A., Variano, E.A., Collision of oil droplets with marine aggregates: Effect of droplet size, *Journal of Geophysical Research: Oceans*, 121, 5, pp. 3250-3260, 2016

The authors quantify the collision of oil droplets and marine aggregates using existing collision rate equations. Results show that interaction of drops and aggregates can substantially influence the drop size distribution, but like all such processes this result is sensitive to the local concentration of oil and aggregates. The analysis also shows that as the size distribution of oil droplets shifts toward larger droplets, a greater fraction of the total oil volume collides with marine aggregates. This result is robust to a variety of different assumptions in the collision model. Results also show that there is not always a dominant collision mechanism. For example, when droplets and aggregates are both close to 10 µm in radius, shear and differential settling contribute nearly equally to the collision rate.

Lanotte, A.S., Corrado, R., Palatella, L., Pizzigalli, C., Schipa, I., Santoleri, R., Effects of vertical shear in modelling horizontal oceanic dispersion, *Ocean Science*, 12, 1, pp. 207-216, 2016

Lanotte et al. (2016) investigated the effect of vertical shear on the horizontal dispersion properties of passive tracer particles on the continental shelf of the South Mediterranean using observation and model data. In situ current measurements reveal that vertical gradients of horizontal velocities in the upper mixing layer decorrelate quite fast (~1/ day), whereas an eddy-permitting ocean model, such as the Mediterranean Forecasting System, tends to overestimate such decorrelation time because of finite resolution effects. Horizontal dispersion, simulated by the Mediterranean Sea Forecasting System, is mostly affected by: (1) unresolved scale motions, and mesoscale motions that are largely smoothed out at scales close to the grid spacing; (2) poorly resolved time variability in the profiles of the horizontal velocities in the upper layer. For the case study they have analysed, they show that a suitable use of deterministic kinematic parametrizations is helpful to implement realistic statistical features of tracer dispersion in two and three dimensions. The approach here suggested provides a functional tool to control the horizontal spreading of small organisms or substance concentrations, and is thus relevant for marine biology, pollutant dispersion as well as oil spill applications.

Laorrattanasak, S., Rongsayamanont, W., Khondee, N., Paorach, N., Soonglerdsongpha, S., Pinyakong, O., Luepromchai, E., Production and Application of Gordonia westfalica GY40 Biosurfactant for Remediation of Fuel Oil Spill, *Water, Air, and Soil Pollution*, 227, 9, p. 325, 2016

The authors produce and apply a biosurfactant from *Gordonia westfalica* GY40 for enhancing fuel oil solubilization and degradation in seawater. The immobilization of G. westfalica GY40 cells on chitosan flakes increased biosurfactant yield, and they achieved a biosurfactant concentration as high as 1.85 g/L when using 2 % soybean oil as the carbon source. The critical micelle dilution (CMD) value of cell-free broth was 25 % and the lowest surface tension was 35 mN m−1. The cell-free broth was able to solubilize and disperse fuel oil, at efficiencies corresponding to biosurfactant concentrations and CMD values. The surface activity of cell-free broth was stable under wide ranges of salinity, temperature, and pH. For the oil degradation test, cell-free broth at 0.5× CMD was added along with polyurethane foam-immobilized Gordonia sp. JC11, an efficient oil-degrading bacterial inoculum, to fuel oil spiked seawater. The system removed 81 % of 1 g/L fuel oil in nutrient seawater medium within 6 days. When tested with three seawater samples collected along the Thai coastal area, the addition of both biosurfactant and immobilized Gordonia sp. JC11 was able to remove 60–70 % of 1 g /L fuel oil, while the natural attenuation (control) removed only 26–35 % of fuel oil. The application of cell-free broth reduced the extraction and purification steps.

Laramore, S., Krebs, W., Garr, A., Effects of Macondo canyon 252 oil (Naturally and Chemically Dispersed) on larval crassostrea virginica (Gmelin, 1791), *Journal of Shellfish Research*, 33, 3, pp. 709-718, 2014

The researchers conducted a series of acute and sub-lethal experiments to examine the potential effects of exposure to water-accommodated fractions (WAFs) of Macondo Canyon 252 crude oil and chemically-enhanced (Corexit 9500A dispersant) water-accommodated fractions (CEWAFs) on embryogenesis, larval development, growth, and survival of the eastern oyster, *Crassostrea virginica*. Nominal exposure concentrations for acute experiments were 0, 100, 200, 400, 800 and 1,200 mg/L for WAFs, and 0, 6.25, 12.5, 25, 50, 100, and 200 mg/L for CEWAFs. Calculated total polycyclic aromatic hydrocarbon (TPAH) values were 0, 22.5, 45, 90, 181, and 271 μg/L for WAFs, and 0, 4.5, 8.9, 17.8, 35.7, 71, and 142 μg/L for CEWAFs. The exposure concentration for sub-lethal experiments was 16 mg/L CEWAF. Total polycyclic aromatic hydrocarbon concentrations represent moderate to high levels of TPAH reported during the Deepwater Horizon (DWH) event. Exposure to acute concentrations of 1 or both of these contaminants was shown to decrease fertilization success (≥100 mg/L CEWAF), hinder trochophore (≥100 mg/L WAF, ≥12.5 mg/L CEWAF) and D-stage (≥200 mg/L WAF, ≥25 mg/L CEWAF) development, increase the risk of D-stage developmental abnormalities (≥100 mg/L WAF, ≥100 mg/L CEWAF), and decrease survival of D-stage (1,092 to 261.8 mg/L WAF, 24-96 h LC50; 177.6 to 24.8 mg/L CEWAF, 24-96 h LC50) and eyed (81.9 to 14.5 mg/L CEWAF; 24-96 h LC50) larvae. Exposure to CEWAFs, in general, resulted in increased toxicity over WAFs, likely as a result of the increased bioavailability of hydrocarbons. In contrast to acute exposures, short-term (24-h) sub-lethal exposure of D-stage larvae to CEWAFs (16 mg/L) had no impact on survival or growth. Concentrations used represent possible TPAH exposure levels based on maximum reported values.

Lewan, M.D., Warden, A., Dias, R.F., Lowry, Z.K., Hannah, T.L., Lillis, P.G., Kokaly, R.F., Hoefen, T.M., Swayze, G.A., Mills, C.T., Harris, S.H., Plumlee, G.S., Asphaltene content and composition as a measure of Deepwater Horizon oil spill losses within the first 80 days, *Organic Geochemistry*,75, pp. 54-60, 2014

The composition and content of asphaltenes in spilled and original wellhead oils from the Deepwater Horizon (DWH) incident provide information on the amount of original oil lost and the processes most responsible for the losses within the first 80 days of the active spill. These can provide a conservative marker for various aspects of mass balance calculations. Spilled oils were collected from open waters, coastal waters and coastal sediments during the incident. Asphaltenes are the most refractory component of crude oils but their alteration in the spilled oils during weathering prevents them from being used directly as a conservative component to calculate original oil losses. The alteration is reflected by their increase in oxygen content and depletion in ^{12}C. Reconnaissance experiments involving evaporation, photo-oxidation, microbial degradation, dissolution, dispersion and burning indicate that the combined effects of photo-oxidation and evaporation are responsible for these compositional changes. Based on measured losses and altered asphaltenes from these experiments, a mean of 61±3vol% of the original oil was lost from the surface spilled oils during the incident. This mean percentage of original oil loss is considerably larger than previous estimates of evaporative losses based on only gas chromatography (GC) amenable hydrocarbons (32-50 vol%), and highlights the importance of using asphaltenes, as well as GC amenable parameters in evaluating original oil losses and the processes responsible for the losses.

Lewis, K., Kaczmarski, A., Lowery, R., Stanga, H., Kallaway, K., Subsea Well Response Project enhances international well incident intervention capabilities, *Proceedings of the Annual Offshore Technology Conference*, 3, pp. 1952-1961, 2014

The authors describe the Subsea Well Response Project (SWRP) was established in 2011 o to further improve subsea well capping response readiness and to further study the need for, and feasibility of, global containment solutions. Through SWRP, international oil and gas companies have worked together on an unprecedented scale to share knowledge, expertise and best practices to enhance international subsea well incident intervention capabilities and to minimise the environmental impact in the event of a subsea well control incident.

Li, P., Chen, B., Li, Z.L., Jing, L., ASOC: A novel agent-based simulation-optimization coupling approach-algorithm and application in offshore oil spill responses, *Journal of Environmental Informatics*, 28, 2, pp. 90-100, 2016a

This study developed an agent-based simulation-optimization approach to provide decisions for device combination and allocation during offshore oil spill recovery in a fast, dynamic and cost-efficient manner under uncertain conditions. Meanwhile, the proposed approach aimed at providing operation control schemes for different devices, reflecting the site conditions, and correspondingly adjusting the global planning in a real-time manner. Such functions would be extremely helpful in the harsh environments prevailing in offshore Newfoundland. In the case study, the developed approach was applied to determine the allocation of 3 responding vessels in collecting spilled oil at 7 locations. The routes of the responding vessels for response operation were optimized and reflected by the principle agent-based programming. Furthermore, several oil weathering processes (e.g., evaporation and dispersion) were also taken into account in the optimization. The modeling results indicated that a minimal timeframe of 21 hours was needed for vessel allocation and recovery operation, leading to an oil recovery rate of 90%. By taking evaporation and dispersion into account, the optimal time window was 18 hours, leading to an oil recovery rate of 75%, an evaporation rate of 12%, and a dispersion rate of 3%.

Li, P., Chen, B., Zhang, B., Liang, J., Zheng, J., Monte Carlo simulation-based dynamic mixed integer nonlinear programming for supporting oil recovery and devices allocation during offshore oil spill responses, *Ocean and Coastal Management*, 89, pp. 58-70, 2014

Li et al. (2014) developed a Monte Carlo simulation-based dynamic mixed integer nonlinear programming (MC-DMINP) approach to provide decisions for devices allocation and recovery operation in a fast, dynamic and cost-efficient manner. In a case study, regression models were developed to simulate the efficiencies of three types of drum skimmers based on the past performance evaluation tests. The models were further integrated with the simulation of oil weathering processes and the optimization method. Finally, the uncertainties in slick area, temperature, and wind speed were also involved in the case study. The optimization results without the consideration of uncertainty indicated a 79.3% of oil recovery efficiency. Meanwhile, 18.5% of the spilled oil was evaporated and 2.1% was dispersed. With the consideration of uncertainties, the mechanical collection of oil still had a major contribution to the transport and fate of oil. Negative effects on mechanical collection and positive effects on evaporation were observed from the uncertainties associated with slick area and temperature. The uncertainties of wind speed had positive effects on dispersion.

Li, P., Weng, L., Niu, H., Robinson, B., King, T., Conmy, R., Lee, K., Liu, L., Reynolds number scaling to predict droplet size distribution in dispersed and undispersed subsurface oil releases, *Marine Pollution Bulletin*, 113, 02-Jan, pp. 332-342, 2016b

This study tested the applicability of modified Weber number scaling with Alaska North Slope (ANS) crude oil, and developing a Reynolds number scaling approach for oil droplet size prediction for high viscosity oils. Dispersant-to-oil-ratio and empirical coefficients were also quantified. Finally, a two-step Rosin-Rammler scheme was introduced for the determination of droplet size distribution. This new approach appeared more advantageous in avoiding the inconsistency in interfacial tension measurements, and consequently delivered concise droplet size prediction. Calculated and observed data correlated well based on Reynolds number scaling. The relation indicated that chemical dispersant played an important role in reducing the droplet size of ANS under different seasonal conditions. The proposed Reynolds number scaling and two-step Rosin-Rammler approaches provide a concise, reliable way to predict droplet size distribution.

Li, Z., Spaulding, M., French, McCay, D., Crowley, D., Payne, J.R., Development of a unified oil droplet size distribution model with application to surface breaking waves and subsea blowout releases considering dispersant effects, *Marine Pollution Bulletin*, 114, 1, pp. 247-257, 2017

An oil droplet size model was developed for turbulent conditions based on non-dimensional analysis of disruptive and restorative forces, which is applicable to oil droplet formation under both surface breaking-wave and subsurface-blowout conditions, with or without dispersant application. This was accomplished using a Weber number formulation and restricting droplet size distributions. This model was calibrated and validated with droplet size data obtained from controlled laboratory studies of dispersant-treated and non-treated oil in subsea dispersant tank tests and field surveys.

Li, Z., Spaulding, M.L., French-McCay, D., An algorithm for modeling entrainment and naturally and chemically dispersed oil droplet size distribution under surface breaking wave conditions, *Marine Pollution Bulletin*, in press, 2017

Li et al. developed a surface oil entrainment model and droplet size model to estimate the flux of oil under surface breaking waves. Both equations are expressed in dimensionless Weber number (We) and Ohnesorge number (Oh, which explicitly accounts for the oil viscosity, density, and oil-water interfacial tension). Data from controlled lab studies, large-scale wave tank tests, and field observations have been used to calibrate the constants of the two independent equations. Predictions using the new algorithm compared well with the observed amount of oil removed from the surface and the sizes of the oil droplets entrained in the water column. Simulations with the new algorithm, implemented in a comprehensive spill model, show that entrainment rates increase more rapidly with wind speed than previously predicted based on the existing Delvigne and Sweeney's (1988) model, and a quasi-stable droplet size distribution ($d < \sim 50.\ \mu m$) is developed in the near surface water.

Liu, T., Sheng, Y., Three dimensional simulation of transport and fate of oil spill under wave induced circulation, *Marine Pollution Bulletin*, 80, 02-Jan, pp. 148-159, 2014

An oil spill model is developed and coupled to a current-wave model to simulate oil spill transport in aquatic environments where waves are present. The oil spill model incorporates physical-chemical processes of oil spill, and simulates oil slick transport by a circulation-driven Lagrangian Parcel model. Using the coupled oil spill model and the current-wave model CH3D-SWAN, a laboratory observed wave induced circulation and oil slick development are successfully simulated, while different current-wave coupling schemes generate different flow patterns and oil slick evolution. The modeling system is also shown to simulate Langmuir circulation and resulting oil slicks. Hypothetical scenarios of oil spill near Virginia coast during Hurricane Isabel and Irene are simulated using the oil spill model and the CH3D-Storm Surge Modeling System to assess the role of storm waves during oil spill. The spill area is significantly larger when storm waves are considered, implying waves significantly increase oil spill dispersion.

Liu, Y.-Z., Roy-Engel, A.M., Baddoo, M.C., Flemington, E.K., Wang, G., Wang, H., The impact of oil spill to lung health-Insights from an RNA-seq study of human airway epithelial cells, Gene, 578, 1, pp. 38-51, 2016

The authors evaluated the transcriptomic profile of human airway epithelial cells grown under treatment of crude oil, the dispersants Corexit 9500 and Corexit 9527, and oil-dispersant mixtures. They identified a very strong effect of Corexit 9500 treatment, with 84 genes (response genes) differentially expressed in treatment vs. control samples. They found an interactive effect of oil-dispersant mixtures; while no response gene was found for Corexit 9527 treatment alone, cells treated with Corexit 9527 +. oil mixture showed an increased number of response genes (46 response genes), suggesting a synergic effect of 9527 with oil on airway epithelial cells. Through GO (gene ontology) functional term and pathway-based analysis, they identified upregulation of gene sets involved in angiogenesis and immune responses and downregulation of gene sets involved in cell junctions and steroid synthesis as the prevailing transcriptomic signatures in the cells treated with Corexit 9500, oil, or Corexit 9500 + oil mixture. Interestingly, these key molecular signatures coincide with important pathological features observed in common lung diseases, such as asthma, cystic fibrosis and chronic obstructive pulmonary disease. The study provides mechanistic insights into the detrimental effects of oil and oil dispersants to the respiratory system and suggests significant health impacts of the recent BP oil spill to those involved in the cleaning operation.

Liu, Y.-Z., Zhang, L., Roy-Engel, A.M., Saito, S., Lasky, J.A., Wang, G., Wang, H., Carcinogenic effects of oil dispersants: A KEGG pathway-based RNA-seq study of human airway epithelial cells, *Gene*, 602, pp. 16-23, 2017

Liu et al. (2017) performed RNA-seq analyses of a system of human airway epithelial cells treated with the BP crude oil and/or dispersants Corexit 9500 and Corexit 9527 that were used to help break up the oil spill. Based on the RNA-seq data, they then systemically analyzed the transcriptomic perturbations of the cells at the KEGG pathway level using two pathway-based analysis tools, GAGE (generally applicable gene set enrichment) and GSNCA (Gene Sets Net Correlations Analysis). The results suggested a pattern of change towards carcinogenesis for the treated cells marked by upregulation of ribosomal biosynthesis (hsa03008) ($p = 1.97E-13$), protein processing (hsa04141) ($p = 4.09E-7$), Wnt signaling (hsa04310) ($p = 6.76E-3$), neurotrophin signaling (hsa04722) ($p = 7.73E-3$) and insulin signaling (hsa04910) ($p = 1.16E-2$) pathways under the dispersant Corexit 9527 treatment, as identified by GAGE analysis. Furthermore, through GSNCA analysis, they identified gene co-expression changes for several KEGG cancer pathways, including small cell lung cancer pathway (hsa05222, $p = 9.99E-5$), under various treatments of oil/dispersant, especially the mixture of oil and Corexit 9527. Overall, the results suggested carcinogenic effects of dispersants (in particular Corexit 9527) and their mixtures with the BP crude oil, and provided further support for more stringent safety precautions and regulations for operations involving long-term respiratory exposure to oil and dispersants.

Loh, A., Shim, W.J., Ha, S.Y., Yim, U.H., Oil-suspended particulate matter aggregates: Formation mechanism and fate in the marine environment, *Ocean Science Journal*, 49, 4, pp. 329-341, 2014

Oil suspended particulate matter (SPM) aggregates (OSA) are naturally occurring phenomena where oil droplets and particles interact to form aggregates. This aggregation could aid cleanup processes of oil contaminated waters. When OSA is formed, it makes oil less sticky and would facilitate the dispersion of oil into the water column. Increased oil-water surface contact by OSA formation enhances biodegradation of oil. Its applicability as a natural oil clean-up mechanism has been effectively demonstrated over past decades. There are many factors affecting the formation of OSA and its stability in the natural environment that need to be understood. This review provides a current understanding of (1) types of OSA that could be formed in the natural environment; (2) controlling factors and environmental parameters for the formation of OSA; (3) environmental parameters; and (4) fate of OSA and its applicability for oil spill remediation processes.

Loh, A., Yim, U.H., A review of the effects of particle types on oil-suspended particulate matter aggregate formation, *Ocean Science Journal*, 51, 4, pp. 535-548, 2016

Loh et al. (2014) review oil suspended particulate matter (SPM) aggregates (OSA) which are naturally occurring phenomena where oil droplets and particles interact to form aggregates. This aggregation could aid cleanup processes of oil contaminated waters or complicate matters by sedimentation. When OSA is formed, it makes oil less adhesive and would facilitate the dispersion of oil into the water column. Increased oil-water surface contact by OSA formation may enhance biodegradation of oil. Its applicability as a natural oil clean-up mechanism has been effectively demonstrated over past decades. There are many factors affecting the formation of OSA and its stability in the natural environment that need to be understood.

Long, Y., Wu, C., Jiang, C., Hu, S., Liu, Y., Simulating the impacts of an upstream dam on pollutant transport: A case study on the Xiangjiang river, China, *Water (Switzerland)*, 8, 11, paper no. 516, 2016

Long et al. (2016) constructed a hydraulic water quality model for the lower reaches of the Xiangjiang River, China, using the hydrodynamic module and convective diffusion module of MIKE21. Six pollution incident scenarios were simulated to investigate the transport process of pollutants, as affected by an upstream dam structure, the Changsha Comprehensive Control Project dam (CCCP). Analysis of the results suggests that the CCCP plays an essential role in controlling the transport and transformation of pollutants. With the CCCP, the process of transport is weakened, and the dispersion effect is strengthened. In particular, after the construction of the CCCP, the same amount of upstream discharge leads to lower peak pollutant concentrations and longer pollutant arrival times to each waterworks' intake, thereby alleviating the impact of water pollution incidents. Further, comparative analysis suggests that the role of CCCP is much more significant with lower discharges (e.g., during the dry season), largely due to the higher amount of water quantity within the reach.

MacDonald, I.R., Garcia-Pineda, O., Beet, A., Daneshgar Asl, S., Feng, L., Graettinger, G., French-McCay, D., Holmes, J., Hu, C., Huffer, F., Leifer, I., Muller-Karger, F., Solow, A., Silva, M., Swayze, G., Natural and unnatural oil slicks in the Gulf of Mexico, *Journal of Geophysical Research: Oceans*, 120, 12, pp. 8364- 8380, 2015

MacDonald et al. (2015) applied neural network analysis of satellite SAR images to quantify the magnitude and distribution of surface oil in the Gulf of Mexico from persistent, natural seeps and from the Deepwater Horizon (DWH) discharge. This analysis identified 914 natural oil seep zones across the entire Gulf of Mexico in pre-2010 data. Their ∼0.1 μm slicks covered an aggregated average of 775 km^2. Assuming an average volume of 77.5 m^3 over an 8-24 h lifespan per oil slick, the floating oil indicates a surface flux of 2.5-9.4 × 104 m^3 yr^{-1}. Oil from natural slicks was regionally concentrated: 68%, 25%, 7%, and <1% of the total was observed in the NW, SW, NE, and SE Gulf, respectively. SAR images from 2010 showed that the 87-day DWH discharge produced a surface-oil footprint fundamentally different from background seepage, with an average ocean area of 11,200 km^2 and a volume of 22,600 m^3. Peak magnitudes of oil were detected during equivalent, ∼14 day intervals around 23 May and 18 June, when wind speeds remained <5 m s^{-1}. Over this interval, aggregated volume of floating oil decreased by 21%; area covered increased by 49%, potentially altering its ecological impact. The most likely causes were increased application of countermeasures.

Marcotte, G., Bourgouin, P., Mercier, G., Gauthier, J.-P., Pellerin, P., Smith, G., Onu, K., Brown, C.E., Canadian oil spill modelling suite: An overview, *39th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 1026-1034, 2016

Marcotte et al., (2016) describe the Canadian Oil Spill Modelling Suite (COSMoS). This modelling suite is flexible in all its components, including input of environmental fields (atmospheric, aquatic) and fate and behavior modules. This paper gives a description of COSMoS, including fate algorithms.

Mauduit, F., Domenici, P., Farrell, A.P., Lacroix, C., Le Floch, S., Lemaire, P., Nicolas-Kopec, A., Whittington, M., Zambonino-Infante, J.L., Claireaux, G., Assessing chronic fish health: An application to a case of an acute exposure to chemically treated crude oil, *Aquatic Toxicology*, 178, pp. 197-208, 2016

The primary objective of this study was to develop a methodology to evaluate a fish's capacity to face an exposure to chemically dispersed oil, and characterize the long-term effects. They applied high-throughput, non-lethal challenge tests to assess hypoxia tolerance, temperature susceptibility and maximal swimming speed as proxies for a fish's functional integrity. These whole animal challenge tests were implemented before (1 month) and after (1 month) juvenile European sea bass (Dicentrarchus labrax) had been acutely exposed (48 h) to a mixture containing 0.08 g/L of weathered Arabian light crude oil plus 4% dispersant (Corexit EC9500A). In addition, experimental populations were then transferred into semi-natural tidal mesocosm ponds and correlates of Darwinian fitness (growth and survival) were monitored over a period of 4 months. Results revealed that fish acutely exposed to chemically dispersed oil remained impaired in terms of their hypoxia tolerance and swimming performance, but not in temperature susceptibility for 1 month post-exposure. These functional impairments had no subsequent ecological consequences under mildly selective environmental conditions since growth and survival were not impacted during the mesocosm pond study. Furthermore, the earlier effects on fish performance were presumably temporary because re-testing the fish 10-months post-exposure revealed no significant residual effects on hypoxia tolerance, temperature susceptibility and maximal swimming speed.

McDaniel, L.D., Basso, J., Pulster, E., Paul, J.H., Sand patties provide evidence for the presence of Deepwater Horizon oil on the beaches of the West Florida Shelf, *Marine Pollution Bulletin*, 97, 02-Jan, pp. 67-77, 2015

McDaniel et al. (2015) suggest oil from the DWH spill could have contaminated the West Florida Shelf (WFS). They utilized polycyclic aromatic hydrocarbon (PAH) analysis to determine presence and potential origin of oil contaminants in beach sand patty samples. PAH profiles from WFS beaches were statistically significantly similar to DWH contaminated samples from the Northeast Gulf of Mexico (Gulf Shores, AL; Ft. Pickens, FL). Dioctyl sodium sulfosuccinate (DOSS), a major component of Corexit 9500 dispersant was also detected in the sediments. DOSS concentrations ranged from 1.6 to 5.5 ngg^{-1} dry weight. Additionally, two samples from DWH oil contaminated beaches were acutely toxic and one WFS beach sediment sample was mutagenic. These observations provide support for the theory that DWH oil made its way onto beaches of the WFS.

Mearns, A.J., Reish, D.J., Oshida, P.S., Ginn, T., Rempel-Hester, M.A., Arthur, C., Rutherford, N., Effects of pollution on marine organisms, *Water Environment Research*, 86, 10, pp. 1869-1954, 2014

Mearns, A.J., Reish, D.J., Oshida, P.S., Ginn, T., Rempel-Hester, M.A., Arthur, C., Rutherford, N., Pryor, R, Effects of pollution on marine organisms, *Water Environment Research*, 87, 10, pp. 1718-1816, 2015

Mearns, A.J., Reish, D.J., Oshida, P.S., Morrison, A.M., Rempel-Hester, M.A., Arthur, C., Rutherford, N., Pryor, R., Effects of pollution on marine organisms, *Water Environment Research*, 88, 10, pp. 1693-1807, 2016

These reviews cover selected annual articles on the biological effects of pollutants and human physical disturbances on marine and estuarine plants, animals, ecosystems and habitats. The review, based largely on journal articles, covers field and laboratory measurement activities (bioaccumulation of contaminants, field assessment surveys, toxicity testing and biomarkers) as well as pollution issues of current interest including oil and petroleum, endocrine disrupters, emerging contaminants, wastewater discharges, dredging and disposal, etc. Special emphasis is placed on effects of oil spills and marine debris due largely to the 2010 Deepwater Horizon oil blowout in the Gulf of Mexico. The focus of this review is on effects, not pollutant fate and transport.

Meng, L., Liu, H., Bao, M., Sun, P., Microbial community structure shifts are associated with temperature, dispersants and nutrients in crude oil-contaminated seawaters, *Marine Pollution Bulletin*, 111, 02-Jan, pp. 203-212, 2016

This study tracked structure shifts of bacterial compositions before, during and after crude oil exposure to determine the microbial response. Test of how temperature, dispersants and nutrients affect the composition of microbial communities or their activities of biodegradation in artificial marine environment were carried out. During petroleum hydrocarbons exposure, the composition and functional dynamics of marine microbial communities were altered, favoring bacteria that could utilize oil such as the Proteobacteria, Firmicutes, Actinobacteria and Bacteroidetes phyla. Low temperature decreased bacterial richness and catabolic diversity due to abated enzyme activity. Dispersants change bacterial composition by increasing the population of Chloroflexi, TM6, OP8, Cyanobacteria and Gemmatimonadetes phyla.

Michaelsen, S., Schaefer, J., Peterson, M.S., Fluctuating asymmetry in *Menidia beryllina* before and after the 2010 Deepwater Horizon oil spill, *PLoS ONE*, 10, 2, article # e0118742, 2015

Michaelson et al. (2015) studied fluctuating asymmetry (small, non-random deviations from perfect bilateral symmetry) which is an informative metric sensitive to contaminants that can be used to assess environmental stress levels. For this study, the well-studied and common Gulf of Mexico estuarine fish, *Menidia beryllina*, was used with pre- and post-oil spill collections. Comparisons of fluctuating asymmetry in three traits (eye diameter, pectoral fin length, and pelvic fin length) were made pre- and post-oil spill across two sites (Old Fort Bayou and the Pascagoula River), as well as between years of collection (2011, 2012)-one and two years, respectfully, after the spill in 2010. They hypothesized that fluctuating asymmetry would be higher in post-Deepwater Horizon samples, and that this will be replicated in both study areas along the Mississippi Gulf coast. They also predicted that fluctuating asymmetry would decrease through time after the oil spill as the oil weathered or was removed. Analyses performed on 1135 fish (220 pre- and 915 post Deepwater Horizon) showed significantly higher post spill fluctuating asymmetry in the eye but no difference for the pectoral or pelvic fins. There was also higher fluctuating asymmetry in one of the two sites both pre- and post-spill, indicating observed asymmetry may be the product of multiple stressors. Fluctuating asymmetry decreased in 2012 compared to 2011. Fluctuating asymmetry is a sensitive measure of sub lethal stress, and the observed variability in this study (pre- vs. post-spill or between sites) could be due to a combination of oil, dispersants, or other unknown stressors.

Michel, C., Cazes, L., Eygun, C., Page-Jones, L., Huet, J.Y., LULA exercise: Testing the oil spill response to a deep-sea blow-out, with a unique combination of surface and subsea response techniques, *Society of Petroleum Engineers - International Petroleum Technology Conference 2014, IPTC 2014 - Innovation and Collaboration: Keys to Affordable Energy*, 5, pp. 4254-4272, 2014a

Michel, C., Cazes, L., Eygun, C., Page-Jones, L., Huet, J.Y., LULA large scale oil spill response exercise: A unique opportunity to test a full set of spilled oil monitoring and modeling techniques, *Proceedings - SPE Annual Technical Conference and Exhibition*, 5, pp. 3905-3930, 2014b

The authors describe how they organized and ran a large exercise. The objective was to check the ability to efficiently define, implement and manage the response to a major oil spill resulting from a subsea blow-out, including the mobilization of a new Sub Sea Dispersant Injection device - SSDI kit from Oil Spill Response Ltd (OSRL-Norway).

Moreira, G., Araújo, M.V., De Oliveira Buriti, C.J., Farias Neto, S.R., Lima, A.G.B., Numerical simulation of leakage of oil in a submerged duct and the behavior of oil in a marine environment, *Defect and Diffusion Forum*, 369, pp. 110-115, 2016

The authors study the leakage of behavior in a submerged pipeline carrying oil. They adopted a two-dimensional model based on mass conservation equations, linear momentum and the model k-ϵ standard turbulence. They used the Ansys CFX for meshing with 40,510 hexahedral elements. The results of pressure fields and volumetric fraction of oil are analyzed and discussed.

Moshtagh, B., Hawboldt, K., Production of biodispersants for oil spill remediation in harsh environment using glycerol from the conversion of fish oil to biodiesel, *2014 Oceans - St. John's, OCEANS 2014*, article no. 7003019, 2015

Moshtagh and Hawboldt (2015) study the feasibility of glycerol, derived from the conversion of waste fish oil to biodiesel, as an effective carbon source for the production of biodispersants by indigenous *Rhodococcus erythropolis* and Bacillus subtilis strain. Glycerol, a tribasic alcohol, is a byproduct of the biodiesel production process. Biodiesel is produced via the transesterification reaction of triglycerides in oils or fats and waste oils, with alcohols, in the presence of a homogeneous catalyst (chemical or enzymatic).

Mu, J., Jin, F., Ma, X., Lin, Z., Wang, J., Comparative effects of biological and chemical dispersants on the bioavailability and toxicity of crude oil to early life stages of marine medaka (Oryzias melastigma), *Environmental Toxicology and Chemistry*, 33, 11, pp. 2576-2583, 2014

The authors assessed the bioavailability and chronic toxicity of water-accommodated fractions of crude oil (WAFs) and 2 dispersants plus dispersed crude oil (chemical dispersant+crude oil [CE-WAF] and biological dispersant+crude oil [BE-WAF]) on the early life stages of marine medaka, *Oryzias melastigma*. The results showed that the addition of the 2 dispersants caused a 3- and 4-fold increase in concentrations of total priority polycyclic aromatic hydrocarbons (PAHs) and high-molecular-weight PAHs with 3 or more benzene rings. The chemical and biological dispersants increased the bioavailability (as measured by ethoxyresorufin-O-dethylase activity) of crude oil 6-fold and 3-fold, respectively. Based on nominal concentrations, chronic toxicity (as measured by deformity) in WAFs exhibited a 10-fold increase in CE-WAF and a 3-fold increase in BE-WAF, respectively. When total petroleum hydrocarbon was measured, the differences between WAF and CE-WAF treatments disappeared, and CE-WAF was approximately 10 times more toxic than BE-WAF. Compared with the chemical dispersant, the biological dispersant possibly modified the toxicity of oil hydrocarbons because of the increase in the proportion of 2- and 3-ringed PAHs in water. The chemical and biological dispersants enhanced short-term bioaccumulation and toxicity, through different mechanisms.

Mullin, J.V., A joint industry research programme to improve oil spill response technologies and methodologies for use in the arctic offshore environment, *Society of Petroleum Engineers - SPE International Conference and Exhibition on Health, Safety, Security, Environment, and Social Responsibility*, 2016

This is a review of industry projects to evaluate countermeasures, including dispersants.

Muncaster, S.P., Jacobson, G., Taiarui, M., King, S., Bird, S., Effects of MV Rena heavy fuel oil and dispersed oil on yellowtail kingfish early life stages, *New Zealand Journal of Marine and Freshwater Research*, 50, 1, pp. 131-143, 2016

Yellowtail kingfish (YTK), Seriola lalandi, embryos were exposed in static incubations to the water-accommodated fraction (WAF) of Rena heavy fuel oil as well as a similar preparation treated with the commercial dispersant Corexit 9500. Mortality in WAF treatments generally increased in association with total polycyclic aromatic hydrocarbon (tPAH) concentration over a 24-h period. Physical abnormalities were observed in some of the larvae exposed to WAF for 48 h. There was no survival in dispersed oil treatments after 24 h of exposure. These treatments had greater tPAH concentrations (2–53 μgL^{-1}) than equivalent WAF dilutions (0.2–1.5 μgL^{-1} tPAH). Indications are that significant morbidity is induced in YTK at ecologically relevant tPAH concentrations.

Munro, N., Burroughs, J., Lund, C., Maintaining response readiness for subsea well control incidents, *Society of Petroleum Engineers - SPE Offshore Europe Conference and Exhibition, OE*, 2015

This describes how Oil Spill Response Limited's (OSRL) Subsea Well Intervention Service (SWIS) was formed. SWIS allows industry the capability to better respond to a subsea well-control incident by providing state of the art subsea well intervention equipment.

Murphy, D., Gemmell, B., Vaccari, L., Li, C., Bacosa, H., Evans, M., Gemmell, C., Harvey, T., Jalali, M., Niepa, T.H.R., An in-depth survey of the oil spill literature since 1968: Long term trends and changes since Deepwater Horizon, *Marine Pollution Bulletin*, 113, 02-Jan, pp. 371-379, 2016

Murphy et al. (2016) examined approximately 10% of oil spill literature (1255 of over 11,000 publications) published from 1968 to 2015. They find that, despite its episodic nature, oil spill research is a rapidly expanding field with a growth rate faster than that of science as a whole. There is a massive post-Deepwater Horizon shift of research attention to the Gulf of Mexico, from 2% of studies in 2004–

2008 to 61% in 2014–2015, thus ranking Deepwater Horizon as the most studied oil spill. There is, however, a longstanding gap in research in that only 1% of studies deal with the effects of oil spills on human health.

Murphy, D.W., Xue, X., Sampath, K., Katz, J., Crude oil jets in crossflow: Effects of dispersant concentration on plume behavior, *Journal of Geophysical Research: Oceans*, 121, 6, pp. 4264-4281, 2016

The authors investigate the effects of premixing oil with chemical dispersant at varying concentrations on the flow structure and droplet dynamics within a crude oil jet transitioning into a plume in a crossflow. The study was motivated by the need to determine the fate of subsurface oil after a well blowout. The laboratory experiments consist of flow visualizations, in situ measurements of the time evolution of droplet-size distributions using holography, and particle image velocimetry to characterize dominant flow features. Increasing the dispersant concentration dramatically decreases the droplet sizes and increases their number, and accordingly, reduces the rise rates of droplets and the upper boundary of the plume. The flow within the plume consists primarily of a pair of counterrotating quasi-streamwise vortices (CVP) that characterize jets in crossflows. It also involves generation of vertical wake vortices that entrain small droplets under the plume. The evolution of plume boundaries is dominated by interactions of droplets with the CVP. The combined effects of vortex-induced velocity and significant quiescent rise velocity of large (∼5 mm) droplets closely agree with the rise rate of the upper boundary of the crude oil plume. Conversely, the much lower rise velocity of the smaller droplets in oil-dispersant mixtures results in plume boundaries rising at rates that are very similar to those of the CVP center. The size of droplets trapped by the CVP is predicted correctly using a trapping function, which is based on a balance of forces on a droplet located within a horizontal eddy.

Nepstad, R., Størdal, I.F., Brönner, U., Nordtug, T., Hansen, B.H., Modeling filtration of dispersed crude oil droplets by the copepod *Calanus finmarchicus*, *Marine Environmental Research*, 105, pp. 1-7, 2015

Nepstad et al. (2015) used a modeling approach to estimate potential ingestion amounts by copepod filtration of oil droplets. The new model was implemented in the OSCAR (Oil Spill Contingency and Response) software suite, and tested for a series of oil spill scenarios and key parameters. Among these, the size of the filtered droplets was found to be the most important factor influencing the model results. Given the assumptions and simplifications of the model, filtration of dispersed crude oil by C. finmarchicus was predicted to affect the fate of 1-40% of the total released oil mass, depending on the release scenario and parameter values used, with the lower end of that range being more probable in an actual spill situation.

Niu, H., Li, P., Yang, R., Wu, Y., Lee, K., Effects of chemical dispersant and seasonal conditions on the fate of spilled oil – modelling of a hypothetical spill near Saint John, NB, *Water Quality Research Journal of Canada*, 51, 3, pp. 233-245, 2016

This study attempts to describe a modelling effort to understand the probable distribution of petroleum hydrocarbons in Port Saint John following a hypothetical release of crude oil to which dispersant is applied during different seasons. A three-dimensional model was used to simulate the transport of oil with a release of 1,000 m^3 of Arabian light crude in the summer and winter. A stochastic approach took into account the uncertainties of environmental inputs. The results were a significant reduction of oil ashore, and enhanced biodegradation with dispersant application. However, these effects were accompanied by an increase of oil in the sediment and water column, which is a concern.

Nordtug, T., Olsen, A.J., Salaberria, I., Øverjordet, I.B., Altin, D., Størdal, I.F., Hansen, B.H., Oil droplet ingestion and oil fouling in the copepod *Calanus finmarchicus* exposed to mechanically and chemically dispersed crude oil, *Environmental Toxicology and Chemistry*, 34, 8, pp. 1899-1906, 2015

Nordtug et al. (2015) investigated the rates of ingestion of oil microdroplets and oil fouling in the zooplankton filter-feeder (*Calanus finmarchicus* at 3 concentrations of oil dispersions ranging from 0.25 mg/L to 5.6 mg/L. To compare responses to mechanically and chemically dispersed oil, the copepods were exposed to comparable dispersions of micron-sized oil droplets made with and without the use of a chemical dispersant (similar oil droplet size range and oil concentrations) together with a constant supply of microalgae for a period of 4 d. The filtration rates as well as accumulation of oil droplets decreased with increasing exposure concentration. The estimated total amount of oil associated with the copepod biomass for the two lowest exposures in the range 11 mL/kg to 17 mL/kg, was significantly higher than the approximately 6 mL/kg found in the highest exposure. For the two lowest concentrations, the filtration rates were significantly higher in the presence of chemical dispersant. Furthermore, a significant increase in the amount of accumulated oil in the presence of dispersant was observed in the low exposure group.

Nørregaard, R.D., Gustavson, K., Møller, E.F., Strand, J., Tairova, Z., Mosbech, A., Ecotoxicological investigation of the effect of accumulation of PAH and possible impact of dispersant in resting high Arctic copepod *Calanus hyperboreus*, *Aquatic Toxicology*, 167, pp. 1-11, 2015

Nørregaard et al. (2015) caught resting high Arctic C. hyperboreus in Disko Bay at >250 meters depth, November 2013, and subsequent experimental work was initiated immediately after, at nearby Arctic Station at Disko Island Western Greenland. C. hyperboreus females were incubated in phenanthrene (111, 50 and 10 nM), pyrene (57, 28 and 6 nM) and benzo(a) pyrene (10, 5 and 1 nM) for three days in treatments with and without oil (corn oil) and dispersant (AGMA DR372). After exposure, the highest measured concentrations of respectively phenanthrene, pyrene and benzo(a) pyrene in the copepods were 129, 30 and 6 nmol PAH g /female. Results showed that with addition of oil and dispersant to the water, the accumulation of PAH was significantly reduced, due to the deposition of the PAHs in the oil phase, decreasing the available PAHs for copepod uptake. While PAH metabolites and a depuration of the PAHs were observed, the copepods still contained PAHs after 77 days of incubation in clean seawater. Differences of treatments with and without oil and dispersant on the egg production were not statistically conclusive, although it is the most likely an effect of the highly variable day-to-day egg production between individual copepods. Equally, although there was an indication that the addition of dispersant and oil increased the mortality rate, there was no statistical difference.

North, E.W., Adams, E.E., Thessen, A.E., Schlag, Z., He R., Socolofsky, S.A., Masutani, S.M., Peckham, S.D., The influence of droplet size and biodegradation on the transport of subsurface oil droplets during the Deepwater Horizon spill: A model sensitivity study, Environmental Research Letters, 10, 2, #24016, 2015

North et al. (2015) evaluated the influence of initial droplet size and rates of biodegradation on the subsurface transport of oil droplets, specifically those from the Deepwater Horizon oil spill. A three-dimensional coupled-model was employed with components that included analytical multiphase plume, hydrodynamic and Lagrangian models. Oil droplet biodegradation was simulated based on first order decay rates of alkanes. The initial diameter of droplets (10-300 μm) spanned a range of sizes expected from dispersant-treated oil. Results indicate that model predictions are sensitive to biodegradation processes, with depth distributions deepening by hundreds of meters, horizontal distributions decreasing by hundreds to thousands of kilometers, and mass decreasing by 92-99% when biodegradation is applied compared to simulations without biodegradation. In addition, there are two- to four-fold changes in the area of the seafloor contacted by oil droplets among scenarios with different biodegradation rates. The spatial distributions of hydrocarbons predicted by the model with biodegradation are similar to those observed in the sediment and water column, although the model predicts hydrocarbons to the northeast and east of the well where no observations were made.

Nwaizuzu, C., Joel, O.F., Sikoki, F.D., Evaluation of oil spill dispersants with a focus on their toxicity and biodegradability, *Society of Petroleum Engineers - SPE Nigeria Annual International Conference and Exhibition, NAICE 2015*, 2015

Nwaizuzu et al. (2015) reviewed literature on oil spill dispersants from 1994-2014 focusing on their toxicity and biodegradability. From the review, many researchers reported that dispersed oil is more toxic than the crude oil while very few were able to show that the dispersed oil was less toxic or equal in toxicity to the crude oil. They also showed that the dispersant increased the concentration of PAHs in the water column, this some attributed to be the cause of the increased toxicity. The effect of the toxicity on the various organs of the organism was noted as some recorded lesions on the gills of fish, drop in heart rate and so on. Many studies suggested that dispersants do actually increase the biodegradability although to some it was restricted to some components of the crude oil. Some researchers however showed that the dispersant reduced the biodegradability of the crude oil. Also noted was the fact that various crude oils reacted differently when mixed with a dispersant. Aquatic organisms reacted differently to different combinations of the dispersed oil. Temperature was shown to play a role in rate of biodegradability.

Nwaizuzu, C., Joel, O.F., Sikoki, F.D., Synergistic effects of dispersed bonny light crude oil on selected aquatic organisms, *Society of Petroleum Engineers - SPE Nigeria Annual International Conference and Exhibition*, 2016

Nwaizuzu et al. (2016) investigated the toxicological effects of OSD Seacare and Bonny light crude oil on the African Catfish (*Clarias gariepinus*). The 96-hr acute toxicity of the water accommodated fraction (WAF) of the mixture of OSD Seacare and Bonny light crude oil was investigated as well as the critical body residue on the fingerlings of the African Catfish. The mean weight and height of the fish was 1.27 g and 5.35 cm respectively. The following concentrations, 30, 90, 180 and 270 ml/L, were used for the CEWAF test. The LC_{50} for the CEWAF was determined to be 199 ml/L while no death was recorded in the WAF test. The oil spill dispersant Seacare increased the toxicity of the crude oil on the test organism by more than 4.5 times further proving that oil spill dispersants can increase the toxicity of crude oil on aquatic organisms. There was no PAH recorded in the fish from the control. From the fish exposed to 30 ml/L of the dispersed oil concentration, the total PAH concentration was 0.73 ppm with 1 Benzo (g,h,i) perylene accounting for the total amount. Whereas the total PAH in the fish exposed to the 270 ml/L concentration was 2.5 ppm with Naphthalene accounting for the total amount. After the acute toxicity testing and the test organisms were put in clean water, it was noticed that the test organisms exposed to the dispersed oil had a change in colour and there was reduced feeding in both those exposed to the WAF of the crude oil and dispersed oil.

Nyankson, E., Gupta, R.B., Effectiveness of three-surfactant dispersants in oil spill remediation, *Engineering Sciences and Fundamentals 2014 - Core Programming Area at the 2014 AIChE Annual Meeting*, 2, #1250, 2014

No further information available.

Nyankson, E., Decuir, M.J., Gupta, R.B., Soybean Lecithin as a Dispersant for Crude Oil Spills, *ACS Sustainable Chemistry and Engineering*, 3, 5, pp. 920-931, 2015a

Nyankson et al. (2015) studied Soybean lecithin, a surface-active agent in the food industry. In addition to its emulsification properties, it is biodegradable, less toxic than the traditional chemical dispersants, and ecologically acceptable. In this study, soybean lecithin was used to formulate dispersants for crude oil spill application. Soybean lecithin was fractionated into phosphatidylinositol (PI) and phosphatidylcholine (PC) enriched fractions using ethanol. The fractionated PI was de-oiled and characterized with Fourier transform infrared spectroscopy (FT-IR). The crude soybean lecithin (CL) and the fractionated PI and PC were solubilized in water and their dispersion effectiveness determined using the U.S. EPA's baffled flask test. The dispersion effectiveness of these solubilized dispersants was compared with that of solid crude lecithin (SL). The dispersion effectiveness of PC was found to be higher than those of SL, CL, and PI at all the surfactant-to-oil ratios (SORs) tested. However, when the fractionated PI was modified or "functionalized" (FPI) with additional hydroxyl groups to alter the hydrophilic-lipophilic balance (HLB), its dispersion effectiveness improved remarkably and was higher than that of PC. At higher SORs (>28 mg/g), the dispersion effectiveness of FPI was slightly higher than that of solubilized DOSS and Tween 80 in propylene glycol. The dispersion effectiveness of PC and FPI on Texas (TC) and light crude (LC) oil samples were almost the same. PC and FPI performed better at the higher salinity of 3.5 wt % than the lower salinities of 0.8 and 1.5 wt %.

Nyankson, E., Olasehinde, O., John, V.T., Gupta, R.B., Surfactant-Loaded Halloysite Clay Nanotube Dispersants for Crude Oil Spill Remediation, *Industrial and Engineering Chemistry Research*, 54, 38, pp. 9328-9341, 2015b

Nyankson et al. (2015b) used halloysite clay nanotubes (HNTs) loaded with different surfactants for crude oil spill remediation. The effectiveness of HNT loaded with the surfactants Tween 80, dioctyl sodium sulfosuccinate (DOSS, D), Span 80 (S) and modified soybean lecithin phosphatidylinositol (Lecithin FPI, LFPI) in crude oil spill remediation was examined with the U.S. EPA's baffled flask test. The release kinetics of the surfactants from the HNT were studied. Ternary diagrams (Span 80-DOSS-Tween 80, Lecithin FPI-DOSS-Tween 80 and Lecithin FPI-Tween 80-Span 80) for the dispersion effectiveness of the surfactant-loaded HNT were then generated. 99 vol % dispersion effectiveness was attained by HNT loaded with ternary food grade surfactants Span 80, Tween 80 and Lecithin FPI.

Nyankson, E., Demir, M., Gonen, M., Gupta, R.B., Interfacially-Active Hydroxylated Soybean Lecithin Dispersant for Crude Oil Spill Remediation, *ACS Sustainable Chemistry and Engineering*, 4, 4, pp. 2056-2067, 2016a

The researchers examined the ability of dispersants formulated with hydroxylated soybean lecithin solubilized in water to disperse crude oil. Soybean lecithin was fractionated and de-oiled. The de-oiled soybean lecithin was hydroxylated and solubilized in water to form the dispersant. The oil-in-water emulsion formed with the hydroxylated soybean lecithin dispersant was stable over a longer period of time and had smaller and more regular shaped oil droplets than the un-hydroxylated soybean lecithin. The interfacial activity of the formulated dispersants was also examined. Generally, the interfacial activity of the soybean lecithin was improved through hydroxylation. Using the U.S. EPA's baffled flask test, the hydroxylated soybean lecithin resulted in a near complete dispersion effectiveness. The improved interfacial activity of the hydroxylated soybean lecithin over the un-hydroxylated counterpart was attributed to the additional hydroxyl groups from the hydroxylation process (i) reducing the rigidity of the fatty acid chain, (ii) increasing interaction between the surfactant and aqueous film at the interface, and (iii) increasing the hydrophilicity of soybean lecithin.

Nyankson, E., Rodene, D., Gupta, R.B., Advancements in Crude Oil Spill Remediation Research after the Deepwater Horizon Oil Spill, *Water, Air, and Soil Pollution*, 227, pp. 1-29, 2016b

The authors review progress in oil spills since the Deepwater Horizon spill, focusing on dispersants and the possibility of making new ones.

Ojala, J., Sirviö, J.A., Liimatainen, H., Nanoparticle emulsifiers based on bifunctionalized cellulose nanocrystals as marine diesel oil-water emulsion stabilizers, *Chemical Engineering Journal*, 288, pp. 312-320, 2016

Ojala et al. (2016) carry out the preparation and properties of marine diesel oil-in-water (o/w) emulsion stabilized by bifunctionalized cellulose nanocrystals (But-CNCs). Bifunctional But-CNCs containing both carboxylic and n-butylamino groups were obtained using partial, sequential periodate-chlorite oxidation and reductive amination, followed by a homogenization treatment to liberate individualized nanocrystals with amphiphilic characteristics. The fabricated But-CNC suspensions were optically transparent, and the nanocrystals that were isolated were rod-like, with lengths ranging between 35 and 120 nm and with lateral dimensions varying from 2 to 4 nm. Bifunctionalized CNCs at low concentrations (up to 0.45 wt%) were investigated as possible surface-active stabilizers in o/w emulsions. In particular, their ability to enhance the emulsification of marine diesel oil in an aqueous environment was addressed in order to evaluate their potential to be used as "green" oil spill response agents.

Oliveira, B.L.A.D., Netto, T.A., Assad, L.P.D.F., Three-dimensional oil dispersion model in the Campos Basin, Brazil, *Environmental Technology (United Kingdom)*, pp. 1-11, 2017

Oliveira et al. describe the physical and mathematical formulation of a three-dimensional oil dispersion model that calculates the trajectory from the seafloor to the sea surface, its assumptions and constraints. Oil dispersion is calculated through two computational routines. The first calculates the vertical dispersion along the water column and resamples the droplets when the oil reaches the surface. The second calculates the surface displacement of the spill. This model is based on the Eulerian approach, and it uses numerical solution schemes in time and in space to solve the equation for advective–diffusive transport. A case study based on an actual accident that happened in the Campos Basin, in Rio de Janeiro state, considering the instant spill of 1000 m^3 was used to evaluate the proposed model. After calculating the vertical transport, it was estimated that the area covered by the oil spill on the surface was about 35,685 m^2. After calculating the dispersion at the surface, the plume area was estimated as 20% of the initial area, resulting in a final area of 28,548 m^2.

Olsen, G.H., Coquillé, N., Le Floch, S., Geraudie, P., Dussauze, M., Lemaire, P., Camus, L., Sensitivity of the deep-sea amphipod Eurythenes gryllus to chemically dispersed oil, Environmental Science and Pollution Research, 23, 7, pp. 6497-6505, 2016

Olsen et al. assessed the sensitivity of a macro-benthic deep-sea organism to dispersed oil. A toxicity test was performed on the macro-benthic deep-sea amphipod (*Eurythenes gryllus*) to determine the concentration causing lethality to 50 % of test individuals (LC_{50}) after an exposure to dispersed Arabian Light oil. The LC_{50} (24 h) was 101 and 24 mg/L after 72 h and 12 mg/L at 96 h. Based on the EPA scale of toxicity categories to aquatic organisms, an LC_{50} (96 h) of 12 mg/L indicates that the dispersed oil was slightly to moderately toxic to E. gryllus.

Olson, G.M., Gao, H., Meyer, B.M., Miles, M.S., Overton, E.B., Effect of Corexit 9500A on Mississippi Canyon crude oil weathering patterns using artificial and natural seawater, *Heliyon*, 3, 3, e00269, 2017

Olson et al. (2017) used replicate laboratory microcosms to conduct weathering experiments to study the weathering of oil and the effects of dispersants on oil weathering. Fresh MC252 oil was evaporatively weathered 40% by-weight to approximate the composition of oil seen in surface slicks during the 2010 spill. This surface oil was then well mixed with two types of seawater, autoclaved artificial seawater, the abiotic control, and Gulf of Mexico seawater, the biotic experiment. Four different weathering combinations were tested: 10 mg of oil mixed in 150 ml artificial seawater (OAS) or natural (i.e., GoM) seawater (ON) and 10 mg of oil with dispersant mixed with 150 ml of artificial seawater (OASD) or natural seawater (OND). For the treatments with dispersant (OASD and OND), the dispersant-to-oil ratio was 1:20. The experiment was carried out over 28 days with replicates that were sacrificed on Days 0, 0.5, 3, 7, 14, 21 and 28. For the OAS and OASD treatments, abiotic weathering (i.e., evaporation) dominated the weathering process. However, the ON and OND treatments showed a dramatic and rapid decrease in total concentrations of both alkanes and aromatics with biodegradation dominating the weathering process. Further, there were no identifiable differences in the observed weathering patterns between microcosms using oil or oil treated with dispersant. In the biotic weathering microcosms, the relative degree of individual polycyclic aromatic hydrocarbon (PAH) depletion decreases with an increase in rings and within a homolog series (increased alkylation). The n-C17/pristane and n-C18/phytane ratios rapidly decreased compared to the abiotic weathering experiments. The C2-dibenzothiophenes (DBT)/C2-phenanthrenes (D2/P2) and C3-DBTs/C3-phenanthrenes (D3/P3) ratios initially remained constant during the early stages of weathering and then increased with time showing preferential weathering of the sulfur containing compounds compared to similar sized PAH compounds. These ratios in the abiotic microcosms remained constant over 28 days. Additionally, twenty-four quantitative MC252 oil biomarker ratios were evaluated to determine if their usefulness as oil source-fingerprinting tools were compromised after significant weathering and dispersant augmentation.

Omar, M.Y., Hassan, A.A., Algthami, M.A., Hegazy, E.H., Oil spill risk assessment (case study), *Developments in Maritime Transportation and Exploitation of Sea Resources - Proceedings of IMAM 2013, 15th International Congress of the International Maritime Association of the Mediterranean*, 2, pp. 841-845, 2014

Omar et al. (2014) used a predictive mathematical oil spill model to simulate the worst oil spill case scenarios in front of the loading and discharge terminal at Jeddah Islamic Port at the Kingdom of Saudi Arabia using different oil types (Arabian heavy and Arabian light crude oil). The model fed with worst meteorological conditions data of year 2010. The study presented the trajectory of the spilled oil slick and its fate (total area of slick, volume of slick, emulsion water content, rate of evaporation and rate of natural dispersion). Conclusion and recommendations related to the oil spill risks, preparedness and response issues were studied based on the model outputs

Ortmann, A.C., Lu, Y.H., Initial community and environment determine the response of bacterial communities to dispersant and oil contamination, *Marine Pollution Bulletin*, 90, 02-Jan, pp.106-114, 2015

Ortmann and Lu (2015) characterized the short-term response of coastal bacteria to dispersant, oil and dispersed oil was characterized using 16S rRNA gene tags in two mesocosm experiments conducted two months apart. Despite differences in the amounts of oil-derived alkanes across the treatments and experiments, increases in the contributions of hydrocarbon degrading taxa and decreases in common estuarine bacteria were observed in response to dispersant and/or oil. Between the two experiments, the direction and rates of changes in particulate alkane concentrations differed, as did the magnitude of the bacterial response to oil and/or dispersant. Together, the data underscore large variability in bacterial responses to hydrocarbon pollutants, implying that bioremediation success varies with starting biological and environmental conditions

Otero-Díaz, L., Pierini, J.O., Chambel-Leitao, P., Malhadas, M., Ribeiro, J., Chambel-Leitao, J., Restrepo, J., Three-dimensional oil spill transport and dispersion at sea by an event of blowout [Transporte y dispersión tridimensional de un derrame de petróleo en el mar debido a un evento "blowout"], *DYNA (Colombia)*, 81, 186, pp. 42-50, 2014

Otero-Diaz et al. 2014 simulated droplet trajectories using the 3-D model at a Caribbean oil platform blowout which showed that droplets with a diameter of 50 μm formed a distinct subsurface plume, which was transported horizontally and could remain below the surface. This plume could have a very restricted area of impact because the dispersion is only controlled by the ocean currents which, at 1000 m depth, have a low intensity and are quite turbulent. In this case, the formed plume stayed trapped at 1000 m depth, not posing a risk to the Caribbean Coast. In contrast, droplets with diameters of 250 μm, 1 and 10 mm rose rapidly to the surface, even with different velocities (6, 10, 20 ms^{-1}).

Overholt, W.A., Marks, K.P., Romero, I.C., Hollander, D.J., Snell, T.W., Kostka, J.E., Hydrocarbon-degrading bacteria exhibit a species-specific response to dispersed oil while moderating ecotoxicity, *Applied and Environmental Microbiology*, 82, 2, pp. 518-527, 2016

Overholt et al. (2016) utilized two environmentally relevant species of hydrocarbon-degrading bacteria to quantify the response to Macondo crude oil and Corexit 9500A-dispersed oil in terms of bacterial growth and oil degradation potential. In addition, specific hydrocarbon compounds were quantified in the dissolved phase of the medium and linked to ecotoxicity using a U.S. Environmental Protection Agency-approved rotifer assay. Bacterial treatment significantly and drastically reduced the toxicity associated with dispersed oil (increasing the 50% lethal concentration [LC_{50}] by 215%). The growth and crude oil degradation potential of Acinetobacter were inhibited by Corexit by 34% and 40%, respectively; conversely, Corexit significantly enhanced the growth of Alcanivorax by 10% relative to that in undispersed oil. Furthermore, both bacterial strains were shown to grow with Corexit as the sole carbon and energy source. Hydrocarbon-degrading bacterial species demonstrate a unique response to dispersed oil compared to their response to crude oil, with potentially opposing effects on toxicity. While some species have the potential to enhance the toxicity of crude oil by producing biosurfactants, the same bacteria may reduce the toxicity associated with dispersed oil through degradation or sequestration.

Owoseni, O., Nyankson, E., Zhang, Y., Adams, D.J., He, J., Spinu, L., McPherson, G.L., Bose, A., Gupta, R.B., John, V.T., Interfacial adsorption and surfactant release characteristics of magnetically functionalized halloysite nanotubes for responsive emulsions, *Journal of Colloid and Interface Science*, 463, pp. 288-298, 2016

Owoseni et al. (2016) describe magnetically responsive oil-in-water emulsions stabilized by a halloysite nanotube supported superparamagnetic iron oxide nanoparticle system. The attachment of the magnetically functionalized halloysite nanotubes at the oil-water interface imparts magnetic responsiveness to the emulsion and provides a steric barrier to droplet coalescence leading to emulsions that are stabilized for extended periods. Interfacial structure characterization by cryogenic scanning electron microscopy reveals that the nanotubes attach at the oil-water interface in a side on-orientation. The tubular structure of the nanotubes is exploited for the encapsulation and release of surfactant species that are typical of oil spill dispersants such as dioctyl sulfosuccinate sodium salt and polyoxyethylene (20) sorbitan monooleate. The magnetically responsive halloysite nanotubes anchor to the oil-water interface stabilizing the interface and releasing the surfactants resulting in reduction in the oil-water interfacial tension. The synergistic adsorption of the nanotubes and the released surfactants at the oil-water interface results in oil emulsification into very small droplets (less than 20 μm).

Özgökmen, T.M., Chassignet, E.P., Dawson, C.N., Dukhovskoy, D., Jacobs, G., Ledwell, J., Garcia-Pineda, O., MacDonald, I.R., Morey, S.L., Olascoaga, M.J., Poje, A.C., Reed, M., Skancke, J., Over what area did the oil and gas spread during the 2010 Deepwater Horizon oil spill? *Oceanography*, 29, 3, pp. 96-107, 2016

Özgökmen et al. (2016) summarizes observations of hydrocarbon dispersion collected at the surface and at depth and the current understanding of the factors that affect the dispersion, as well as the improved ability to model and predict oil and gas transport. As a direct result of studying the area where oil and gas spread during the DWH oil spill, the forecasting capabilities have been greatly enhanced. State-of-the-art oil spill models now include the ability to simulate the rise of a buoyant plume of oil from sources at the seabed to the surface. A number of efforts have focused on improving the understanding of the influences of the near-surface oceanic layer and the atmospheric boundary layer on oil spill dispersion, including the effects of waves. In the future, oil spill modeling routines will likely be included in Earth system modeling environments, which will link physical models (hydrodynamic, surface wave, and atmospheric) with marine sediment and biogeochemical components.

Ozhan, K., Parsons, M.L., Bargu, S., How were phytoplankton affected by the Deepwater Horizon oil spill? *BioScience*, 64, 9, pp. 829-836, 2014

Ozhan et al. did a literature review of phytoplankton responses to the Macondo (Deepwater Horizon) oil spill indicate that the phytoplankton may have been stimulated by the oil spill, although the presence of low-salinity water in the region makes it difficult to discount the importance of riverine-borne nutrients as a factor. A few studies suggest that the oil spill was toxic to some phytoplankton species, whereas others indicate that the degree of tolerance to the oil or to dispersants differs among species. These results generally comply with findings of previous studies, but a lack of published field data analyses prevents further assessment of the impacts of the Deepwater Horizon oil spill on phytoplankton population dynamics in the northern Gulf of Mexico.

Pan, Z., Zhao, L., Boufadel, M.C., King, T., Robinson, B., Conmy, R., Lee, K., Impact of mixing time and energy on the dispersion effectiveness and droplets size of oil, *Chemosphere*, 166, pp. 246-254, 2017

Pan et al. studied effects of mixing time and energy on Alaska Northern Slope (ANS) and diluted bitumen Cold Lake Blend (CLB) were investigated using EPA baffled flask test, with the non-standard method using colorimetry. Dispersion effectiveness and droplet size distribution were measured after 5–120 min. A modeling method to predict the mean droplet size was introduced for the first time to tentatively elucidate the droplet size breakup mechanism. The ANS dispersion effectiveness greatly increased with dispersant and mixing energy. However, little CLB dispersion was noted at small energy input. With dispersant, the ANS droplet size distribution reached quasi-equilibrium within 10 min, but that of CLB seems to reach quasi-equilibrium after 120 min. Dispersants are assumed ineffective on high viscosity oils because dispersants do not penetrate them. The authors provide an alternative explanation based on the elongation time of the droplets and its residence in high intensity zones. When mixing energy is small, CLB did not disperse after 120 min, long enough to allow the surfactant penetration.

Parra-Guevara, D., Skiba, Y.N., Modeling the discharge of nutrients for bioremediation of oil-polluted marine environments: Linear and quadratic programming strategies, *Bioremediation: Processes, Challenges and Future Prospect*s, pp. 121-167, 2014

Parra-Guevara and Skiba (2014) model biodegradation as two variational problems, along with the corresponding linear and quadratic programming problems, with the aim to determine optimal discharge point and optimal discharge rate of a nutrient to be released to a marine environment polluted with oil. The objective is to minimize the total discharge of nutrient into the system provided that their concentrations still reach critical values sufficient to eliminate oil residuals in affected zones through bioremediation. A tridimensional problem for the advection-diffusion equation and its corresponding model are used to simulate, estimate and control the dispersion of nutrient in a limited region. In each oil-polluted zone, the mean concentration of nutrient is determined by means of an integral formula in which the corresponding model solution serves as a weight function for discharge rate and initial distribution of the nutrient. Critical values of such mean concentrations are used as the constraints of variational and programming problems (linear and quadratic). In the quadratic variational problem, the analytical expression for determining the optimal discharge rate of nutrient is given as a linear combination of certain values of the resulting solutions calculated for all the zones under consideration. Through this expression, a function has been obtained, whose minimum value is achieved at the optimal point of discharge. In the linear variational problem, some additional constraints are posed to limit not only the local discharge of nutrient, but also the mean concentration of this substance in the whole region. The ability of both methods is demonstrated by numerical experiments on the remediation in an oil-polluted channel by using three control zones. In particular, the experiments with the linear programming problem show that the optimal discharge rate can always be obtained with a simple combination of step functions.

Parsa, R., Kolahdoozan, M., Alavi Moghaddam, M.R., Mid-depth oil concentration due to vertical oil dispersion in a regular wave field, *Environmental Fluid Mechanics*, 16, 2, pp. 335-346, 2016a

Parsa et al. (2016a) investigate the vertical oil dispersion of surface oil spills in a regular wave field in a wave tank. Various waves characteristics and different volumes of oil spills are tested to assess the oil concentration variations at two sampling stations. It is found that the oil concentration due to vertical oil dispersion follows an ascending diagram to reach a maximum and then decreases while oil slick passes the location. The maximum mid-depth oil concentration at the farther sampling station is 30–50 % less than the concentration at the closer sampling station to the spill location. A 50 % increase in oil spill volume causes 30–60 % growth in oil concentrations. The relations between oil concentration and important parameters such as wave characteristics, amount of spilled oil and the distance of sampling stations from the spill location are indicated and also oil concentration variations are quantified. Two equations are derived through statistical analysis of the obtained experimental data, which estimate the magnitude and time of maximum oil concentration.

Parsa, R., Kolahdoozan, M., Moghaddam, M.R.A., Vertical oil dispersion profile under non-breaking regular waves, *Environmental Fluid Mechanics*, 16, 4, pp. 833-844, 2016B

Parsa et al. (2016b) investigate vertical oil dispersion of surface oil spills under non-breaking regular waves in a wave tank. The variation in oil concentration caused by oil dispersion in a water column was studied to determine the vertical oil dispersion profile. The experiments were performed using different waves characteristics for different volumes of oil spill to evaluate the variation in oil concentration at three depths at two sampling stations. The correlations between oil concentration and the main parameters of wave characteristics, oil spill volume, sampling depth, and distance of sampling stations to spill location were assessed. The results revealed that the trend of variation in oil concentration versus wave steepness is linear. The results obtained from experimental measurements indicated that the oil concentrations at mid-depth were 44–77 % and the concentrations near the flume bed were 12–33 % of the concentration near the water surface.

Passow, U., Formation of rapidly-sinking, oil-associated marine snow, *Deep-Sea Research Part II: Topical Studies in Oceanography*, 129, pp. 232-240, 2016

Significant amounts of oil accumulated at the sea surface and in a subsurface plume during the Deepwater Horizon spill in the Gulf of Mexico (GoM) in 2010. A substantial fraction of this oil was removed from the marine environment by mechanical recovery or burning, or it reached shorelines, whereas another fraction remained within the marine environment, where it dispersed (chemically or naturally), emulsified or sedimented. After the DwH accident the sedimentation of hydrocarbons to the seafloor via rapidly sinking, oil-associated marine snow has become a focus of attention, and it has been hypothesized that marine snow formation significantly impacted the distribution of the oil from the DwH spill. Roller table experiments are presented that investigated the conditions inducing the formation of oil-associated marine snow, focusing especially on the effects of oil type, photochemical aging of oil, and the presence of phytoplankton or dispersant. Large, mucus-rich marine snow, termed microbial marine snow, formed in treatments incubated with the oil that had accumulated at the sea surface. This bacteria-mediated formation of up to cm-sized marine snow in the absence of particles >1 μm, represents a unique formation pathway different from that of the physical coagulation of particles. Microbial marine snow, albeit smaller, also formed in the presence of crude oil that had been aged for ≥3 weeks in sunlight, but no particles formed in the presence of unaltered crude. The dispersant Corexit 9500A (Corexit:oil ratio=1:100) impeded the formation of microbial marine snow, requiring a re-evaluation of the benefits and detriments of Corexit 9500A as a mediating measure. Phytoplankton aggregates also incorporated fossil carbon, providing an alternate pathway for the formation of oil-associated marine snow. The ubiquitous formation and rapid sedimentation of oil-rich marine snow can explain the high accumulation rate of flocculent material at the seafloor and on corals observed after the DwH spill.

Passow, U., Ziervogel, K., Marine snow sedimented oil released during the Deepwater Horizon spill, *Oceanography*, 29, 3, pp. 118-125, 2016

During and after the Deepwater Horizon (DWH) spill in the northern Gulf of Mexico, a massive amount of oil compounds and marine particles, termed floc, accumulated on the seafloor. It is now well established that sedimentation of oil following the DWH spill occurred largely in association with marine oil snow (MOS), a term that became accepted as describing marine snow that incorporates oil. A significant amount of the spilled oil made its way to the seafloor as MOS, appreciably affecting the distribution of oil within the ocean. This article summarizes current knowledge of the different types of MOS that sank, and the underlying processes that led to MOS formation as well as to the sedimentation and deposition of oil on the seafloor during and after the DWH spill.

Patra, P., Somasundaran, P., Multipronged Approach for Oil Spill Remediation, O*il Spill Remediation: Colloid Chemistry-Based Principles and Solutions*, pp. 175-188, 2014

Patra and Somasundaran (2014) review surfactants employed for phase separation that can potentially be used effectively to disperse oil. New greener surfactants that have been shown to adsorb on minerals and disperse/flocculation have potential to replace some of the relatively toxic oil dispersants. In this regard, understanding of the structure-property-performance relationships of greener bioreagents is helpful for addressing problems associated with dispersion. These problems include toxicity related issues such as that resulting from the use of petroleum based dispersants. Plant derived biosurfactants for oil dispersion are examined.

Peiffer, R.F., Cohen, J.H., Lethal and sublethal effects of oil, chemical dispersant, and dispersed oil on the ctenophore *Mnemiopsis leidyi*, *Aquatic Biology*, 23, 3, pp. 237-250, 2015

Peiffer and Cohen (2015) established the lethal levels for water-accommodated fractions of Corexit 9500A chemical dispersant, crude oil (WAF), and dispersed crude oil (CEWAF) for the ctenophore *Mnemiopsis leidyi* at both 15 and 23°C. This gelatinous zooplankter was sensitive to dispersant at both temperatures, as well as to oil solutions, with some increase in toxicity of CEWAF as compared to WAF. Subsequent sublethal assays for routine respiration rate, bioluminescence, and glutathiones- transferase activity were conducted on individuals surviving 24 h exposures to test solutions at both 15 and 23°C. GST activity increased significantly in 2.5 and 5 mg/L dispersant solutions at 15°C, suggesting a metabolic detoxification response to the dispersant-containing solutions, but no effect of any solution type on routine respiration rate was observed. Light emission through mechanically stimulated bioluminescence and photocyte lysis decreased with exposure to crude oil WAF and CEWAF at both temperatures and to dispersant exposure at 23°C. Collectively, these results demonstrate that M. leidyi exhibits both lethal and sublethal effects from acute crude oil exposure, with an elevation of some sublethal responses upon addition of chemical dispersant. Sublethal effects of oil and dispersants in pelagic species, most notably impairment of luminescence, should be considered when evaluating oil spill response strategies.

Pendergraft, M.A., Rosenheim, B.E., Varying relative degradation rates of oil in different forms and environments revealed by ramped pyrolysis, *Environmental Science and Technology*, 48, 18, pp. 10966-10974, 2014

Pendergraft and Rosenheim (2014) employed a ramped pyrolysis carbon isotope technique to investigate thermochemical and isotopic changes in organic material from coastal environments contaminated with oil from the 2010 BP Deepwater Horizon oil spill. Oiled beach sediment, tar ball, and marsh samples were collected from a barrier island and a brackish marsh in southeast Louisiana over a period of 881 days. Stable carbon (^{13}C) and radiocarbon (^{14}C) isotopic data demonstrate a predominance of oil-derived carbon in the organic material. Ramped pyrolysis profiles indicate that the organic material was transformed into more stable forms. The data indicate relative rates of stabilization in the following order, from fastest to slowest: high energy beach sediments > low energy beach sediments > marsh > tar balls. Oil was transformed most rapidly where shoreline energy and the rates of oil dispersion and exchange with water, sediments, microbes, oxygen, and nutrients were greatest. Still, isotope data reveal persistence of oil.

Perhar, G., Arhonditsis, G.B., Aquatic ecosystem dynamics following petroleum hydrocarbon perturbations: A review of the current state of knowledge, *Journal of Great Lakes Research*, 40, S3, pp. 56-72, 2014

Perhar and Arhonditsis (2014) review crude oil spills in aquatic environments. They note toxic effects cascade across trophic levels, affecting phytoplankton, zooplankton, fish, aquatic birds, mammals, and benthic organisms. The literature shows much work has been done detailing the toxicity of crude oil at each of the aforementioned trophic levels, but very little of this knowledge has been incorporated into modelling studies. Instead, the majority of contemporary models focus on the abiotic fate of spilled crude oil, driven by factors such as evaporation, dissolution, dispersion, sinking, and sedimentation. In this study, they present a thorough review of the role of crude oil toxicity on aquatic organisms from a food web point of view, followed by an overview of the modelling literature, and finally outline a modelling plan in which they aim to fill the biological/ecological gap in contemporary oil spill models.

Pi, G., Mao, L., Bao, M., Li, Y., Gong, H., Zhang, J., Preparation of Oil-in-Seawater Emulsions Based on Environmentally Benign Nanoparticles and Biosurfactant for Oil Spill Remediation, *ACS Sustainable Chemistry and Engineering*, 3, 11, pp. 2686-2693, 2015

Pi et al used tetradecane and crude oil-in-seawater emulsions with silica nanoparticles modified in situ with rhamnolipid. The interactions of silica particles with rhamnolipid were characterized by contact angle, interfacial tension, TEM, and SEM measurements. The images of confocal fluorescence microscopy and SEM showed the oil droplet microstructure and the morphology of nanoparticles at the oil droplet-water interface. The average emulsion droplet size and emulsion index were investigated. These results indicated a synergistic stabilization upon rhamnolipid addition. The synergy was even more efficient in the case of seawater with a high salinity. Here, because of the strong flocculation caused by high salinity, silica nanoparticles alone were not an effective emulsifier in seawater. The modification of silica nanoparticles by rhamnolipid changed the contact angle and promoted their adsorption at the oil-seawater interface, which provided an efficient barrier to droplet coalescence. The emulsification of rhamnolipid-modified silica nanoparticles worked well in crude oil-seawater systems.

Pi, G., Li, Y., Bao, M., Mao, L., Gong, H., Wang, Z., Novel and Environmentally Friendly Oil Spill Dispersant Based on the Synergy of Biopolymer Xanthan Gum and Silica Nanoparticles, *ACS Sustainable Chemistry and Engineering*, 4, 6, pp. 3095-3102, 2016

The authors report on the development of a Pickering emulsifier based on the synergy of natural biopolymer, Xanthan Gum (XG), and silica nanoparticles.

Pie, H.V., Mitchelmore, C.L., Acute toxicity of current and alternative oil spill chemical dispersants to early life stage blue crabs (*Callinectes sapidus*), *Chemosphere*, 128, pp. 14-20, 2015

Pie and Mitchelmore (2015) examined the acute toxicity of five oil spill chemical dispersants on the blue crab Callinectes sapidus. Static, non-renewal 48 h acute toxicity tests were performed on stage-II blue crab zoea. The median lethal concentration (LC_{50}) was calculated for each dispersant at 24 h and 48 h using nominal concentrations for each dispersant tested. The 48 h LC_{50} values from the most to the least toxic ranged from 10.1 mg/L for Dispersit SPC 1000 to 76.5 mg/L for Orca. For all dispersants, the swimming activity and mobility of larvae decreased with increasing dispersant concentration within 24 h of exposure and reached relative immobility at concentrations below LC_{50} values. These results show that the dispersants examined in this study are only slightly toxic after 48 h exposure to the earliest life stage of blue crabs that might likely be exposed to dispersants in the environment, with the exception of Dispersit SPC 1000 that bordered between slightly and moderately toxic. Although the dispersants themselves appear to not cause substantial acute toxicity, sublethal and potentially delayed impacts, such as, reduced mobility or food source availability could indirectly remove larvae from the population and need to be further examined, as do larval responses in standard chronic toxicity tests.

Pietroski, J.P., White, J.R., DeLaune, R.D., Effects of dispersant used for oil spill remediation on nitrogen cycling in Louisiana coastal salt marsh soil, *Chemosphere*, 119, pp. 562-567, 2015

Marsh soil samples were collected from an unimpacted marsh site proximal to coastal areas that suffered light to heavy oiling for a laboratory evaluation to determine the effect of Corexit on the wetland soil microbial biomass as well as N-mineralization and denitrification rates. Microbial biomass nitrogen (N) values were below detection for the 1:10, 1:100 and 1:1000 Corexit:wet soil treatments. The potentially mineralizable N (PMN) rate correlated with microbial biomass with significantly lower rates for the 1:10 and 1:100 Corexit:wet soil additions. Potential denitrification rates for Corexit:wet soil ratios after immediate dispersant exposure were below detection for the 1:10 treatment, while the 1:100 was 7.6 ± 2.7% of the control and the 1:1000 was 33 ± 4.3% of the control. The 1:10. 000 treatment was not significantly different from the control. Denitrification rates measured after two weeks exposure to the surfactant found the 1:10 treatment still below detection limit and the 1:100 ratio was 12 ± 2.6% of the control. Results from this lab study suggest that chemical dispersants have the potential to negatively affect the wetland soil microbial biomass and resultant microbial activity. Consequences of exposure led to reductions in several important microbial-regulated ecosystem services including water quality improvement (denitrification) and ecosystem primary productivity (N-mineralization). Future studies should investigate the longer-term impacts of dispersant exposure on the microbial consortia to determine if microbial activity recovers over time.

Place, B.J., Perkins, M.J., Sinclair, E., Barsamian, A.L., Blakemore, P.R., Field, J.A., Trace analysis of surfactants in Corexit oil dispersant formulations and seawater, *Deep-Sea Research Part II: Topical Studies in Oceanography*, 129, pp. 273-281, 2016

Place et al. (2016) review dispersant-in-water analysis. Although the dispersant formulations contain four classes of surfactants, current studies to date have focused on the anionic surfactant, bis-(2-ethylhexyl) sulfosuccinate (DOSS). Factors affecting the integrity of environmental and laboratory samples for Corexit analysis have not been systematically investigated. For this reason, a quantitative analytical method was developed for the detection of all four classes of surfactants, as well as the hydrolysis products of DOSS, the enantiomeric mixture of α- and β-ethylhexyl sulfosuccinate (α-/β-EHSS). The analytical method was then used to evaluate which practices for sample collection, storage, and analysis resulted in high quality data. Large volume, direct injection of seawater followed by liquid chromatography tandem mass spectrometry (LC-MS/MS) minimized analytical artifacts, analysis time, and both chemical and solid waste. Concentrations of DOSS in the seawater samples ranged from 71 to 13,000 ng/L, while the nonionic surfactants including Span 80, Tween 80, Tween 85 were detected infrequently (26% of samples) at concentrations from 840 to 9100 ng/L. The enantiomers α-/β-EHSS were detected in seawater, at concentrations from 200 to 1900 ng/L, and in both Corexit dispersant formulations, indicating α-/β-EHSS were applied to the oil spill and may be not unambiguous indicator of DOSS degradation. Best practices were provided to ensure sample integrity and data quality for environmental monitoring studies and laboratory that require the detection and quantification of Corexit-based surfactants in seawater.

Poje, A.C., Özgökmen, T.M., Lipphardt, Jr. B.L., Haus, B.K., Ryan, E.H., Haza, A.C., Jacobs, G.A., Reniers, A.J.H.M., Olascoaga, M.J., Novelli, G., Griffa, A., Beron-Vera, F.J., Chen, S.S., Coelho, E., Hogan, P.J., Kirwan, Jr. A.D., Huntley, H.S., Mariano, A.J., Submesoscale dispersion in the vicinity of the Deepwater Horizon spill, *Proceedings of the National Academy of Sciences of the United States of America*,111, 35, pp. 12693-12698, 2014

Poje et al. (2014) used surface drifters providing high-frequency position data by the near-simultaneous release of hundreds of accurately tracked. They studied the structure of submesoscale surface velocity fluctuations in the Northern Gulf of Mexico. Observed two-point statistics confirm the accuracy of classic turbulence scaling laws at 200-m to 50-km scales and clearly indicate that dispersion at the submesoscales is local, driven predominantly by energetic submesoscale fluctuations. The results demonstrate the feasibility and utility of deploying large clusters of drifting instruments to provide synoptic observations of spatial variability of the ocean surface velocity field.

Powell, K.C., Chauhan, A., Dynamic interfacial tension and dilational rheology of dispersant Corexit 9500, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 497, pp. 352-361, 2016

Powell and Chauhan measure dynamic interfacial tension and dilational rheology, which have not been previously reported for the Corexit 9500 system. Measurements show that increasing the aqueous salinity to approximately that of sea water drastically increases Corexit 9500s adsorption rates and lowers interfacial tensions. Specifically, the interfacial tension decreases from a pure interface value of 22.4 mN/m to approximately 2 mN/m at 10 wt% Corexit 9500 and 0.01 wt% Corexit 9500 for the fresh and salt water systems, respectively. The time for achieving equilibrium is inversely proportional to the concentration. Dynamic and equilibrium interfacial tensions for both systems are well described by a simplified predictive model for several orders of magnitude in concentration. Finally, moderately high dilational moduli values which are frequency independent and primarily elastic in nature were measured. The time scales for adsorption reported here could be useful in designing the process for spraying the dispersant in deep-sea applications. The model parameters, although not physically correct due to the assumption of a single component system, could be useful in predicting the adsorption of the sprayed dispersant to the rising oil plume.

Prince R.C., Oil spill dispersants: Boon or bane? *Environmental Science and Technology*, 49, 11, pp. 6376-6384, 2015

Prince (2015) provides a very one-side positive review of dispersants with little to back statements up: “Dispersants provide a reliable large-scale response to catastrophic oil spills that can be used when the preferable option of recapturing the oil cannot be achieved. By allowing even mild wave action to disperse floating oil into tiny droplets (<70 μm) in the water column, seabirds, reptiles, and mammals are protected from lethal oiling at the surface, and microbial biodegradation is dramatically increased. Recent work has clarified how dramatic this increase is likely to be: beached oil has an environmental residence of years, whereas dispersed oil has a half-life of weeks. Oil spill response operations endorse the concept of net environmental benefit, that any environmental costs imposed by a response technique must be outweighed by the likely benefits. This critical review discusses the potential environmental debits and credits from dispersant use and concludes that, in most cases, the potential environmental costs of adding these chemicals to a polluted area are likely outweighed by the much shorter residence time, and hence integrated environmental impact, of the spilled oil in the environment.”

Prince, R.C., Coolbaugh, T.S., Parkerton, T.F., Oil dispersants do facilitate biodegradation of spilled oil, *Proceedings of the National Academy of Sciences of the United States of America*, 113, 11, p. E1421, 2016

This is a reply to a criticism of their paper that claims that dispersants facilitate oil biodegradation.

Prince, R.C., Kelley, B.A., Butler, J.D., Dispersants substantially increase biodegradation of otherwise undispersed oil, *Proceedings of the 38th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 715-721, 2015

Prince et al. (2015) apparently show that three dispersants widely available in international stockpiles effectively stimulate biodegradation when compared to oil in floating slicks.

PWS RCAC, Fingas, M., Banta J., Decola, E., *Prince William Sound Dispersants Monitoring Protocol: Implementation and Enhancement of SMART (Special Monitoring of Applied Response Technologies)*, Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Report, Anchorage, Alaska, 49 p., July, 2016

This is a proposed new monitoring protocol to monitor dispersant application for effectiveness. Suggestions for improvements by the many parties who carried out monitoring work on the Deepwater Horizon are incorporated and new concepts advanced to address these suggestions. The primary decision point for making dispersant applications on a particular day is proposed to be a simple field test. This field test involves a simple method with four repetitions. The other protocols are suggested to be in three ‘levels’. Level 1 is an important level involving visual monitoring from an aircraft over the slick. Photographs of effective and not effective dispersant applications are given as a guide. Instructions and points-to-note for this level are given. Level 2 involves towing instruments through the un-dispersed and dispersed slicks at depths of 2 and 5 m. The tow consists of a LISST-100X particle instrument which has an onboard fluorometer (Turner Cyclops-7) and an Aqua Monitor, which is a towed water sampler. A depth meter provides confirmation of sampling depth. The data from the LISST includes an integrated particle count, similar to a Total Petroleum Hydrocarbon (TPH) measurement, and a Volume Mean Diameter (VMD). It is proposed that an effective dispersion results if the integrated particle count (TPH) measurement is at least 10 times the background value and that the VMD is less than 50 µm over a large part of the sample tow. The output of the fluorometer can give confirmation that the particles are oil or not. Water samples are analyzed in the laboratory for TPH and TPAH to confirm field readings. The results of these readings on a particular day and a new field test in the morning would form the basis for a decision for the day's dispersant application. There is Level 3 which consists of taking water samples for further analysis by two different methods. One is using the Payne sampler which provides a separation between particulate and dissolved material. These two samples are analyzed in the laboratory for TPH and TPAH and specific compounds if so desired. Another sample is taken at 2 m and optionally at 5 m using an Alpha sampler. This sample is split into 3 samples, two 1000 mL samples, one for chemical analysis and the other for laboratory toxicity studies. A third smaller split of about 200 mL is used for onboard MicroTox assessment. Several alternate laboratory analyses are also summarized. The improvements over the previous protocols include the use of particle measurement as an indicator of effectiveness rather than fluorescence; the inclusion of a field effectiveness test and use of a towed sampling device.

Prouty, N.G., Fisher, C.R., Demopoulos, A.W.J., Druffel, E.R.M., Growth rates and ages of deep-sea corals impacted by the Deepwater Horizon oil spill, *Deep-Sea Research Part II: Topical Studies in Oceanography*, 129, pp. 196-212, 2016

Prouty et al. continued their study of the impact of the April 2010 Deepwater Horizon spill on deep-sea coral communities in the Gulf of Mexico. Impacts from the spill include observation of corals covered with flocculent material, with bare skeleton, excessive mucous production, sloughing tissue, and subsequent colonization of damaged areas by hydrozoans. Information on growth rates and life spans of deep-sea corals is important for understanding the vulnerability of these ecosystems to both natural and anthropogenic perturbations, as well as the likely duration of any observed adverse impacts. They report radiocarbon ages and radial and linear growth rates based on octocorals (Paramuricea spp. and Chrysogorgia sp.) collected in 2010 and 2011 from areas of the DWH impact. The oldest coral radiocarbon ages were measured on specimens collected 11 km to the SW of the oil spill from the Mississippi Canyon spill site: 599 and 55 calendar years BP, suggesting continuous life spans of over 600 years for Paramuricea biscaya, the dominant coral species in the region. Calculated radial growth rates, between 0.34 µm yr^{-1} and 14.20 µm yr^{-1}, are consistent with previously reported proteinaceous corals from the Gulf. Anomalously low radiocarbon ($\delta^{14}C$) values for soft tissue from some corals indicate that these corals were feeding on particulate organic carbon derived from an admixture of modern surface carbon and a low ^{14}C carbon source. Results from this work indicate fossil carbon could contribute 5-10% to the coral soft tissue $\delta^{14}C$ signal within the area of the spill impact. The influence of a low ^{14}C carbon source (e.g., petro-carbon) on the particulate organic carbon pool was observed at all sites within 30 km of the spill site, with the exception of MC118, which may have been outside of the dominant northeast-southwest zone of impact. The quantitatively assessed extreme longevity and slow growth rates documented here highlight the vulnerability of these long-lived deep-sea coral species to disturbance.

Qi, X., Helmond, I., Crooke, E., Sherlock, M., Ross, A.S., Lee, K., Irving, P., Rapid dispersant effectiveness monitoring equipment for oil spill response, *Proceedings of the 38th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 722-734, 2015

Qi et al. (2015) new monitoring kit to measure dispersant field effectiveness. This kit contains multiple channels of chemical sensors. It is capable of providing in situ monitoring of property change of chemically dispersed oil in addition to overall increase of dispersed oil in water and therefore can yield more quantitative assessment of oil dispersant effectiveness. The towed platform that the sensors are mounted on has the unique flexibility to be deployed in two different modes for fixed depth (~1 m) subsurface water monitoring and water column profiling respectively.

Rabalais, N.N., Turner, R.E., Effects of the Deepwater Horizon oil spill on coastal marshes and associated organisms, *Oceanography*, 29, 3, pp. 150-159, 2016

Rabalais and Turner (2016) synthesize key results of published research on the oiling effects on coastal habitats in the Gulf of Mexico as a result of the DeepWater Horizon spill. There were immediate negative impacts in the moderately to heavily oiled marshes, and on the resident fish and invertebrates. Recovery occurred in many areas within the two years following the oiling and continues, but permanent damage from heavily oiled marshes resulted in eroded shorelines. Organisms, including microbial communities, invertebrates, and vertebrates, were diminished by acute and chronic hydrocarbon exposure. However, the inherent variability in populations and levels of exposure, compounded with multiple stressors, often masked what were expected, predictable impacts. The effects are expected to continue to some degree with legacy hydrocarbons, or the marsh ecosystem will reach a new baseline condition in heavily damaged areas.

Rahsepar, S., Smit, M.P.J., Murk, A.J., Rijnaarts, H.H.M., Langenhoff, A.A.M., Chemical dispersants: Oil biodegradation friend or foe? *Marine Pollution Bulletin,* 108, 1–2, 15 July, pp. 113–119,1016

Rahsepar et al. (2016) study the effect of Corexit on oil biodegradation by alkane and/or aromatic degrading bacterial culture in artificial seawater at different dispersant to oil ratios (DORs). The results show that dispersant addition did not enhance oil biodegradation. At DOR 1:20, biodegradation was inhibited, especially when only the alkane degrading culture was present. With a combination of cultures, this inhibition was overcome after 10 days. This indicates that initial inhibition of oil biodegradation can be overcome when different bacteria are present in the environment. They conclude that the observed inhibition is related to the enhanced dissolution of aromatic compounds into the water, inhibiting the alkane degrading bacteria.

Rao, A., Sathe, M., Reddy, R.K., Nandakumar, K., CFD with population balance model to predict droplet size distribution in submerged turbulent multiphase jets, *Canadian Journal of Chemical Engineering*, 94, 11, pp. 2072-2085, 2016

Rao et al. (2016) present a numerical model for predicting the droplet size distribution resulting from the interaction of turbulent oil jets with the surrounding quiescent environment. They achieve this objective by integrating traditional multiphase CFD models with a population balance approach. The developed model has been validated against the experimental observations reported by Johansen et al. 2013. The 'Mixture model' has been employed for evaluating flow fields in the system. They restrict the study to the atomization regime, where the droplet disintegration process has a greater significance over the competing coalescence mechanism. The population balance equation has been solved using the 'Class method' and the disintegration of droplets has been modelled by including the breakage kernel suggested by Lehr, 2002 The developed model has been used to analyze the effect of dispersed oil phase flow rates, the presence of dispersants, and the presence of air in the jet phase on the overall size distribution of oil droplets. They also present a case which compares the droplet size distributions obtained by using the flow field evaluated by a more rigorous Eulerian Two-Fluid model over Mixture model.

Ransom, J.T., Filbrun, J.E., Hernandez, F.J., Jr., Condition of larval Spanish mackerel Scomberomorus maculatus in relation to the Deepwater Horizon oil spill, *Marine Ecology Progress Series*, 558, pp. 143-152, 2016

Ransom et al. (2016) review Spanish Mackerel in context with the Deepwater Horizon oil spill that coincided with the pelagic larval stages of many valued commercial and recreational fishes in the northern Gulf of Mexico. Larval fish survival and eventual recruitment into adult populations may have been impacted directly through toxicity or indirectly through changes in the planktonic food web caused by the release of oil and chemical dispersants during the DWHOS event. Using samples from a long-term ichthyoplankton survey off the coast of Alabama, USA, in a region impacted by the DWHOS, the abundance and condition of larval Spanish mackerel *Scomberomorus maculatus* were compared during summer months in years before (2007-2009), during (2010) and after (2011) the DWHOS. Changes in larval quality were examined using morphometric and weight-based body condition indices, whereas potential trophic impacts were quantified using stable C and N isotopes. Larval abundance did not differ across years. However, larvae were in better body condition during the DWHOS period relative to before the spill. Larvae had generally similar isotopic values through time. Thus, larval Spanish mackerel body condition was largely resilient to the harmful effects of the DWHOS.

Ratchagar, N., Hemalatha, S., Dispersion of oil spilled under solid ice cover, *World Journal of Engineering*, 11, 5, pp. 495-505, 2014

The researchers developed a model to study the physical dispersion and distribution of oil particle concentration in the presence of Coriolis force of oil spilled under solid ice cover. The movement of oil slick is obtained by employing perturbation technique and the dispersion of oil is studied using generalized dispersion model proposed by Gill (1967). The mean concentration is computed by introducing a slug of finite length separated from pure solvent using suitable impermeable barriers by varying the dimensionless time, axial distance and length of solute slug.

Redman, A.D., Role of entrained droplet oil on the bioavailability of petroleum substances in aqueous exposures, *Marine Pollution Bulletin*, 97, 02-Jan, pp. 342-348, 2015

Redman applies mechanistic fate and effects models to characterize the role of droplet oil on dissolved exposure and predicted effects from both neat and weathered crude oils, and refined fuel oils. The main effect from droplet oil is input of additional dissolved hydrocarbons to the exposure system following preparation of the initial stock solution. Toxicity was characterized using toxic units (TU) and shows that replenishment of bioavailable hydrocarbons by droplets in toxicity tests with low droplet content (e.g., <1. mg/L) is negligible, consistent with typical exposure conditions following open ocean oil spills. Further, the use of volumetric exposure metrics (e.g., mg/L) introduces considerable variability and the bioavailability-based metrics (e.g., TUs) provide a more consistent basis for understanding oil toxicity data.

Redman, A.D., Butler, J.D., Letinski, D.J., Parkerton, T.F., Investigating the role of dissolved and droplet oil in aquatic toxicity using dispersed and passive dosing systems, *Environmental Toxicology and Chemistry*, 36, 4, pp. 1020-1028, 2017

Redman et al. carried out toxicity tests to improve the understanding of the role of droplets, using acute toxicity tests with *Daphnia magna* and *Americamysis bahia* with Endicott crude oil in low-energy mixing systems with and without Corexit 9500 dispersant. Exposures were also prepared by placing crude oil in silicone tubing and passively dosing test media to provide dissolved oil exposures without droplets. A framework was described for characterizing dissolved phase exposures using both mechanistic modeling and passive sampling measurements. The approach is then illustrated by application to data from the present study. Expression of toxicity in terms of toxic units calculated from modeled dissolved oil concentrations or passive sampling measurements showed similar dose responses between exposure systems and organisms, despite the gradient in droplet oil. These results indicate that droplets do not appreciably contribute to toxicity for the two species investigated.

Resnik, D.B., Miller, A.K., Kwok, R.K., Enge, L.S., Sandler, D.P., Ethical issues in environmental health research related to public health emergencies: Reflections on the GuLF STUDY, *Environmental Health Perspectives*, 123, 9, pp. A227-A231, 2015

Resnik et al. explore ethical issues that arose in the Gulf Long-term Follow-up Study (GuLF STUDY) and cleanup workers. Ethical issues encountered by GuLF STUDY investigators included a) minimizing risks and promoting benefits to participants, b) obtaining valid informed consent, c) providing financial compensation to participants, d) working with vulnerable participants, e) protecting participant confidentiality, f) addressing conflicts of interest, g) dealing with legal implications of research, and h) obtaining expeditious review from the institutional review board (IRB), community groups, and other committees. To ensure that ethical issues are handled properly, it is important for investigators to work closely with all agencies during the development and implementation of research and to consult with groups representing the community. Researchers should consider developing protocols, consent forms, survey instruments, and other documents prior to the advent of a public health emergency to allow for adequate and timely review by constituents. When an emergency arises, these materials can be quickly modified to take into account unique circumstances and implementation details.

Restrepo, J.M., Venkataramani, S.C., Dawson, C., Nearshore sticky waters, *Ocean Modelli*ng, 80, pp. 49-58, 2014

Restrepo et al. describe and model why wind- and current-driven flotsam, oil spills, pollutants, and nutrients, approaching the nearshore frequently appear to slow down/park just beyond the break zone, where waves break. Moreover, the portion of these tracers that beach will do so only after a long time. Explaining why these tracers park and at what rate they reach the shore has important implications on a variety of different nearshore environmental issues, including the determination of what subscale processes are essential in computer models for the simulation of pollutant transport in the nearshore. Using a simple model, they provide an explanation for the underlying mechanism responsible for the parking of tracers, not subject to inertial effects, the role played by the bottom topography, and the non-uniform dispersion which leads, in some circumstances, to the eventual landing of all or a portion of the tracers. They refer to the parking phenomenon in this environment as nearshore sticky waters.

Riehm, D.A., McCormick, A.V., The role of dispersants' dynamic interfacial tension in effective crude oil spill dispersion, *Marine Pollution Bulletin*, 84, 02-Jan, pp. 155-163, 2014

Riehm and McCormick measured dispersion effectiveness of dispersants containing Tween 80, Span 80, and dioctyl sodium sulfosuccinate (DOSS) using a modified Swirling Flask test, and was correlated with both initial and dynamic interfacial tension produced by those dispersants at an oil-water interface. Compositional trends in effectiveness were shown to be governed by: (1) initial oil-water interfacial tension observed upon dispersant-oil-saltwater contact; (2) rate of increase (or decrease) from the initial interfacial tension as DOSS was rapidly lost to the aqueous phase; and (3) gradually slowing kinetics of dispersant adsorption to the oil-water interface as Span 80 concentration was increased, which ultimately diminished dispersion effectiveness considerably even as dynamic interfacial tension remained $<10^{-3}$mN/m. It is proposed that this third phenomenon results not only from the hydrophobicity of Span

80, but also from the dependence of mixed Tween-Span-DOSS reverse micelles' stability in crude oil on dispersant composition

Riehm, D.A., Neilsen, J.E., Bothun, G.D., John, V.T., Raghavan, S.R., McCormick, A.V., Efficient dispersion of crude oil by blends of food-grade surfactants: Toward greener oil-spill treatments, *Marine Pollution Bulletin*, 101, 1, pp. 92-97, 2015

Riehm et al. (2015) measured effectiveness of oil spill dispersants containing lecithin/Tween 80 (L/T) blends in ethanol was measured as a function of L:T ratio, surfactant:solvent ratio, solvent composition, and dispersant:oil ratio (DOR) using baffled flask dispersion effectiveness tests. Optimal L:T ratios are between 60:40 and 80:20 (w/w); at higher L:T ratios, effectiveness is limited by high interfacial tension, while at lower L:T ratios, insufficient lecithin is present to form a well-packed monolayer at an oil-water interface. These optimal L:T ratios retain high effectiveness at low DOR: 80:20 (w/w) L:T dispersant is 89% effective at 1:25 DOR (v/v) and 77% effective at 1:100 DOR (v/v). Increasing surfactant:solvent ratio increases dispersant effectiveness even when DOR is proportionally reduced to keep total surfactant concentration dosed into the oil constant. Replacing some of the ethanol with octane or octanol also increases dispersant effectiveness, suggesting that ethanol's hydrophilicity lowers dispersant-oil miscibility, and that more hydrophobic solvents would increase effectiveness.

Riehm, D.A., Rokke, D.J., McCormick, A.V., Water-in-Oil Microstructures Formed by Marine Oil Dispersants in a Model Crude Oil, *Langmuir*, 32, 16, pp. 3954-3962, 2016

Riehm et al. (2016) studied DOSS (dioctyl sodium sulfosuccinate), Tween 80, and Span 80, surfactants commonly used in marine crude oil spill dispersants, and mixed these into a model oil at a total surfactant concentration of 2 wt %, typical for dispersant-treated oil slicks. These surfactant-oil blends also contained 0.5-1.5 wt % synthetic seawater to enable formation of water-in-oil microstructures. Trends in dynamic oil-seawater interfacial tension as a function of surfactant blend composition are similar to those observed in prior work for crude oil treated with similar blends of these surfactants. In particular, Span 80-rich surfactant blends exhibit much slower initial dynamic IFT decline than DOSS-rich surfactant blends in both model oil and crude oil, and surfactant blends containing 50 wt % Tween 80 and a DOSS:Span 80 ratio near 1:1 produce ultralow IFT in the model oil ($<10^{-4}$ mN/m) just as similar surfactant blends do in crude oil. At all DOSS:Span 80 ratios, surfactant blends containing 50 wt % Tween 80 form clear solutions with seawater in the model oil. Cryo-transmission electron microscopy and dynamic light scattering show that these solutions contain spherical W/O microstructures, the size and dispersity of which vary with surfactant blend composition and surfactant:seawater molar ratio. Span 80-rich microstructures exhibit high polydispersity index and large diameters (≥100 nm), whereas DOSS-rich microstructures exhibit smaller diameters (20-40 nm) and low polydispersity index, indicating a narrow microstructure size distribution. The smaller diameters of DOSS-rich microstructures, as well as the fact that DOSS molecules, being oil-soluble, can diffuse to a bulk oil-water interface as monomers much faster than any of these microstructures, may explain why DOSS-rich blends adsorb to the oil-water interface more quickly than Span 80-rich blends, a phenomenon which has been linked in prior work to the higher effectiveness of DOSS-rich Tween/Span/DOSS-based oil dispersants.

Riehm, D.A., Rokke, D.J., Paul, P.G., Lee, H.S., Vizanko, B.S., McCormick, A.V., Dispersion of oil into water using lecithin-Tween 80 blends: The role of spontaneous emulsification, 2017, *Journal of Colloid and Interface Science*, 487, pp. 52-59, 2017

The authors used Lecithin-rich mixtures of the surfactants lecithin and Tween 80 to study oil spill dispersants. These mixtures produce much higher oil-water interfacial tension than comparable dispersants. This suggests interfacial phenomena other than interfacial tension influence lecithin-Tween

80 dispersants' effectiveness. The interface between seawater and dispersant-crude oil mixtures was studied using light microscopy, cryogenic scanning electron microscopy, and droplet coalescence tests. The Lecithin:Tween 80 ratio was varied from 100:0 to 0:100 and wt% dispersant in the oil was varied from 1.25 to 10 wt%. Tween 80-rich dispersants cause oil-into-water spontaneous emulsification, while lecithin-rich dispersants primarily cause water-into-oil spontaneous emulsification. The possible mechanisms for this spontaneous emulsification are discussed. Dispersant loss into seawater due to oil-into-water spontaneous emulsification may explain why Tween 80-rich dispersants are less effective than lecithin-rich dispersants with comparable interfacial tension. However, droplet coalescence times observed for Tween 80-rich dispersant-oil mixtures may mitigate the effects of dispersant leaching.

Rios, M.C., Moreira, Í.T.A., Oliveira, O.M.C., Pereira, T.S., de Almeida, M., Trindade, M.C.L.F., Menezes, L., Caldas, A.S., Capability of Paraguaçu estuary (Todos os Santos Bay, Brazil) to form oil–SPM aggregates (OSA) and their ecotoxicological effects on pelagic and benthic organisms, *Marine Pollution Bulletin*, 114, 1, pp. 364-371, 2017

Rios et al. collected oil and sediment samples from Campos Basin and six stations of Paraguaçu estuary, Todos os Santos Bay, Brazil, to study oil-sediment interaction. The sediments samples were analyzed for organic matter determined by the EMBRAPA method, nitrogen determined by the Kjeldahl method, and phosphorus determined by the method described by Aspila. The oil trapped in OSA was extracted following the method described by Moreira. The experiment showed a relationship between the amount of organic matter and OSA formation and consequently the dispersion of the studied oil. On the basis of the buoyancy of OSA and the ecotoxicological effects on pelagic and benthic community, the priority areas for application of remediation techniques are Cachoeira, Maragogipe, and Salinas da Margarida because of the large amount of oil that accumulated at the bottom of the experiment flask (5.85%, 27.95%, and 38,98%; 4.2%, 17.66%, and 32.64%; and 11.82%, 8.07%, and 10.91% respectively).

Robles, R.R., Serrano, J.P., Sloshing mechanical model for stability and handling qualities evaluation of the C295 aircraft with the OSD system, *29th Congress of the International Council of the Aeronautical Sciences, ICAS 2014*, 2014

Robles and Serrano describe a version of the C295 military aircraft with an Oil Spill Dispersant (OSD) system to be used as an airborne platform capable spraying oil spills. A sloshing mechanical model was developed to evaluate the impact of the dispersant sloshing on the aircraft dynamics. Effects on aircraft stability, handling qualities and Pilot Induced Oscillations sensitivity characteristics were assessed carrying out exhaustive simulations analyses prior to the maiden flight. Sloshing model validation was supported by Computational Fluid Dynamics simulations and a dedicated flight test campaign.

Rongsayamanont, W., Soonglerdsongpha, S., Khondee, N., Pinyakong, O., Tongcumpou, C., Sabatini, D.A., Luepromchai, E., Formulation of crude oil spill dispersants based on the HLD concept and using a lipopeptide biosurfactant, *Journal of Hazardous Materials*, 334, pp. 168-177, 2017

Solvent-free dispersants for crude oil spills were formulated based on the hydrophilic-lipophilic deviation (HLD) concept and using lipopeptides from Bacillus sp. GY19. The lipopeptides were recovered and concentrated from cell-free broth by foam fractionation and freeze-drying. They had good surface activity under varying temperatures, pH and NaCl levels. Moreover, the lipopeptides had low toxicity to copepods (LC_{50} 1174 mg/L) and whiteleg shrimp (LC_{50} 1050 mg/L). The characteristic curvature of the lipopeptides showed that they were more hydrophobic (Cc 4.93) than sodium dihexyl sulfosuccinate (SDHS, Cc −0.92). The HLD equation was used to calculate the lipopeptide and the SDHS fractions in the dispersant formulations according to the equivalent alkane carbon number (EACN) of hydrocarbons and seawater salinity. The molar fraction of lipopeptides increased with increasing EACN. The lipopeptide-SDHS mixtures formed microemulsion Type III with specific hydrocarbons and crude oils. Oil displacement and baffled flask tests showed that the formulations reduced the interfacial tension and solubilized crude oil in the water column at higher efficiency than commercial dispersants or lipopeptides alone. In summary, the effectiveness of the lipopeptide-based dispersant corresponded to the optimal HLD.

Rosenheim, B.E., Pendergraft, M.A., Flowers, G.C., Carney, R., Sericano, J.L., Amer, R.M., Chanton, J., Dincer, Z., Wade, T.L., Employing extant stable carbon isotope data in Gulf of Mexico sedimentary organic matter for oil spill studies, *Deep-Sea Research Part II: Topical Studies in Oceanography*, 129, pp. 249-258, 2016

Rosenheim et al. compiled and mapped available carbon isotope data from sedimentary organic material sampled from the Gulf of Mexico prior to 2010. These data provide a baseline to which any changes in the Gulf of Mexico after the 2010 Deepwater Horizon oil spill can be compared. The mean $\delta^{13}C$ values, relative to PDB, are -21.4 (entire Gulf of Mexico), -21.7 (shelf sediments), -20.4 (Deepwater sediments), and -25.2 (seep-affected sediments). They compare pre-spill mean $\delta^{13}C$ values to carbon isotope measurements of sedimentary organic material from coretop samples collected after the 2010 Deepwater Horizon oil spill. The differences between the mean compiled $\delta^{13}C$ values and the post-spill $\delta^{13}C$ values are corroborated by qualitative relationships with the concentration of polycyclic aromatic hydrocarbons, a proxy for oil contamination, in the sediment. The relationships between $\delta^{13}C$ of the sedimentary organic material and PAH concentrations allow estimation of background levels of PAHs on the shelf and in the deep Gulf of Mexico. Higher background levels of PAH on the shelf likely relate to Mississippi River outflow and its deposition of petrogenic PAH in riverine sediments

Ross, B.J., Hallock, P., Chemical toxicity on coral reefs: Bioassay protocols utilizing benthic foraminifers, *Journal of Experimental Marine Biology and Ecology*, 457, pp. 226-235, 2014

Ross and Hallock developed bioassay protocols for chemical pollutants utilizing *Amphistegina gibbosa d'Orbigny*, the coral species found ubiquitously on Caribbean and western Atlantic reefs. A protocol was developed to identify the 48-h Lethal Concentration LC_{50}, the concentration of a test chemical in seawater that killed 50% of the specimens during 48-h exposure. Two chemicals found in oil dispersants employed in the clean-up efforts in the Gulf of Mexico, propylene glycol and 2-butoxyethanol, were used as test chemicals. Some individuals, which had appeared to be dead at the end of the 48-h exposure period, recovered following rinsing and removal to clean seawater. This observation required further definition of an Acute Concentration AC_{50}, the concentration of chemical in seawater that killed or rendered inactive 50% of the specimens during a 48-hour exposure. They also evaluated several indicators of chronic effects of the short-term exposure. All concentrations of propylene glycol tested resulted in significantly higher incidences of bleaching (color loss in the foraminifers due to loss of, or damage to, algal symbionts). As bleaching is a common stress response in zooxanthellate corals, even short-term exposure to dispersant chemicals may increase susceptibility to bleaching.

Rudder, M.M., Kowlessar-George, G.P., Hosein, R.B., Butcher, S.A., Implications of the response to the la Brea oil spill of 2013 as a result of the first-Time activation of the revised national oil spill contingency plan of 2013 of Trinidad and Tobago, *SPE Latin American and Caribbean Health, Safety, Environment, and Sustainability Conference 2015*, pp. 274-288, 2015

Rudder et al. examine the response measures utilized during the multiple oil spills of December 2013 in Trinidad. In addition, it will explore how successful these response measures were, the adjustments that were made, the challenges with public relations and other factors that negatively impacted the response. Also, a discussion of what technological features would have improved the actual responses to the multiple oil spills with particular reference to the La Brea Oil Spill. Managing the response to this La Brea spill necessitated the use of the Incident Command System (ICS) as required under the NOSCP as well as the activation of the NOSCP to the Tier 3 level. A variety of response equipment and resources such as booms, dispersants, degreasers and shoreline cleaners as well as vessel and aerial surveillance were utilized. The decision to utilize Corexit 9500A in the response elicited national condemnation. In addition, the fact that mangroves were impacted by oil and they were purposely not cleaned received condemnation. There was major dissatisfaction with the mechanisms employed to conduct beach cleaning which prolonged the clean-up. The spill caused disgruntlement amongst the affected residents. The public relations aspect of the response was viewed as lacking timely, coordinated and relevant information in this social media age. There were many lessons learned as a result of the La Brea oil spill. Some of the main lessons were the need for synchronization of the objectives of the various Incident Command Teams; the importance of having a high-technology Emergency Operations Centre; the need for pre-spill trajectory models prior to the incident; the need for early warning systems to detect oil spills when they occur and the need for a Joint Information Centre to manage the media issues. The spill also highlighted the value of the ICS and the use of the ICS forms and the need for synchronized display of such forms over multiple platforms. The La Brea Oil Spill of December 2013 in Trinidad is an example of the challenge of responding to an oil spill incident in the Caribbean region while also considering the unpredictability of the behavior of an oil spill when subjected to environmental conditions. This oil spill, some 7554 barrels of Bunker C, travelled tens of kilometers from its point of origin dominated solely by the prevailing current during the time of the spill. The spill negatively impacted the coastline of La Brea and environs, affecting shorelines, beaches, mangroves and other environmentally sensitive areas, as well as residents and stakeholders

Rung, A.L., Oral, E., Fontham, E., Harrington, D.J., Trapido, E.J., Peters, E.S., Mental Health Impact of the Deepwater Horizon Oil Spill among Wives of Clean-up Workers, *Epidemiology*, 26, 4, pp. e44-e46, 2015

Rung et al. conducted a survey of wives of cleanup workers of the DeepWater Horizon. The prevalence of depression in the sample was 31%, 33% reported increases in domestic fights, 31%–32% reported memory loss post-spill, and 39%–43% reported an inability to concentrate post-spill. An index representing total exposure to the spill, including both direct physical exposure to the oil/dispersants as well as indirect economic impact from the consequences of the oil spill, was constructed from 12 questionnaire items (mean 4.2, out of a possible range of 0–12) and further subdivided into physical exposure (mean score 1.6, out of a possible range of 0–6) and economic exposure indices (mean score 2.4, out of a possible range of 0–6). These results suggest that exposure to the Deepwater Horizon Oil Spill was associated with depression, increase in domestic partner fights, memory loss, and an inability to concentrate among female partners of oil spill clean-up workers.

Salnikov, A.V., Gribov, G.G., The method of determining the effectiveness of dispersant for oil spill response at icy seas, *Society of Petroleum Engineers - SPE Russian Petroleum Technology Conference*, 2015

Salnikov and Gribov propose a new fast method of determination of effectiveness of dispersants for the Arctic seas as developed in Ukhta State Technical University. The method is simple and doesn't demand expensive equipment and highly skilled personnel, and also allows carrying out several parallel experiments.

Sammarco, P.W., Kolian, S.R., Warby, R.A.F., Bouldin, J.L., Subra, W.A., Porter, S.A., Concentrations in human blood of petroleum hydrocarbons associated with the BP/Deepwater Horizon oil spill, Gulf of Mexico, 2016, *Archives of Toxicology,* 90, 4, pp. 829-837, 2016

Sammarco et al. (2016) review hydrocarbons in humans as a result of the DWH spill. During/after the BP/Deepwater Horizon oil spill, cleanup workers, fisherpersons, SCUBA divers, and coastal residents were exposed to crude oil and dispersants. These people experienced acute physiological and behavioral symptoms and consulted a physician. They were diagnosed with petroleum hydrocarbon poisoning and had blood analyses analyzed for volatile organic compounds; samples were drawn 5–19 months after the spill had been capped. The researchers examined the petroleum hydrocarbon concentrations in the blood. The aromatic compounds m,p-xylene, toluene, ethylbenzene, benzene, o-xylene, and styrene, and the alkanes hexane, 3-methylpentane, 2-methylpentane, and iso-octane were detected. Concentrations of the first four aromatics were not significantly different from US National Health and Nutritional Examination Survey/US National Institute of Standards and Technology 95th percentiles, indicating high concentrations of contaminants. The other two aromatics and the alkanes yielded equivocal results or significantly low concentrations. The data suggest that single-ring aromatic compounds are more persistent in the blood than alkanes and may be responsible for the observed symptoms. People should avoid exposure to crude oil through avoidance of the affected region, or utilizing hazardous materials suits if involved in cleanup, or wearing hazardous waste operations and emergency response suits if SCUBA diving. Concentrations of alkanes and PAHs in the blood of coastal residents and workers should be monitored through time well after the spill has been controlled.

Sandoval, K., Ding, Y., Gardinali, P., Characterization and environmental relevance of oil water preparations of fresh and weathered MC-252 Macondo oils used in toxicology testing, *Science of the Total Environment*, 576, pp. 118-128, 2017

The key aim of this study was compare and contrast the physical and chemical compositions of oil water mixtures prepared using fresh and weathered Macondo-related oils under different conditions of mixing and in the presence/absence of chemical dispersants. All samples were assessed for the presence of droplets, droplet size distribution, and detailed chemical composition including polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbon by fluorescence (TPHF). Preparations were also tested for stability over a 96-h period relevant to acute toxicity tests. The results indicate that water accommodated fractions (WAFs) produced consistent, droplet free solutions with concentration that represented the soluble components of the oil used. As expected, chemically-enhanced WAFs (CEWAFs) and high-energy WAFs (HEWAFs) generated large amounts of micron-size droplets and their chemical composition corresponded closely with that of the whole oil. However, the HEWAFs were highly dynamic, and unlike CEWAFs, much of the oil resurfaced within few hours of the initial preparation. Viscosity and lack of dispersability are the limiting factors for preparation of CEWAFs with weathered oils, in contrast HEWAFs did effectively introduce large amounts of weathered oil droplets in the test media. Despite this benefit, droplet sizes significantly decreased in HEWAFs with increase in weathering of the oil creating an additional variable to consider. Because the contribution of small droplets to toxicity is a topic that needs further investigation, the interpretation of results from high-energy preparations needs to be further evaluated. When the TPAHs concentrations of all preparations at all loadings were compared with the publicly available water-column data for samples analyzed during and after the DWH incident response they all ranked above the vast majority of the 10,828 samples reported during the actual spill. This leads to the conclusion that current methods of oil-water preparations are variable and may not be representative of actual conditions.

Santander-Avanceña, S.S., Sadaba, R.B., Taberna, H.S., Jr., Tayo, G.T., Koyama, J., Acute Toxicity of Water-Accommodated Fraction and Chemically Enhanced WAF of Bunker C Oil and Dispersant to a Microalga *Tetraselmis tetrathele*, Bulletin of Environmental Contamination and Toxicology, 96, 1, pp. 31-35, 2016

Santander-Avanceña (2016) assessed the toxicity of water-accommodated fraction (WAF) and chemically enhanced WAF (CEWAF) of bunker C oil and dispersant to a microalga, *Tetraselmis tetrathele*. The 72-h median effective concentration (72-h EC_{50}) of CEWAF and dispersant were determined at 3.30 % and 2.40 %, respectively. The no-observed effect concentration (NOEC) of CEWAF to T. tetrathele was at 2.0 % and lowest observed effect concentration (LOEC) was at 3.0 % while NOEC and LOEC of the dispersant to T. tetrathele were determined at 1.0 % and 2.0 %, respectively. The addition of dispersant to oil increased the amount of total PAH present in the CEWAF test solutions. Dispersant alone was highly toxic, and the toxicity of CEWAF was primarily caused by the presence of dispersant.

Sathiakumar, N., Tipre, M., Turner-Henson, A., Chen, L., Leader, M., Gohlke, J., Post-Deepwater horizon blowout seafood consumption patterns and community-specific levels of concern for selected chemicals among children in Mobile County, Alabama, *International Journal of Hygiene and Environmental Health*, 220, 1, pp. 1-7, 2017

Sathiakumar et al. (2017) characterized risk pertaining to seafood consumption patterns following the Deepwater Horizon oil spill, among school children (K to 4th grade) residing in close proximity to the Gulf of Mexico in Mobile County, Alabama. Responses on seafood consumption pattern including the type of seafood and intake rate during the pre and post oil spill periods, from parents of 55 school children from three schools located <20 mile radius from the Gulf of Mexico shoreline (coastal group) were compared with those from parents of 55 children from three schools located ≥20 miles away from the shoreline (inland group). They also estimated levels of concern (LOCs) in seafood for selected chemicals found in crude oil including heavy metals, and polycyclic aromatic hydrocarbons (PAH), and dioctyl sodium sulfosuccinate (DOSS), the primary compound in dispersants. The coastal group ate more seafood consisting primarily of crustaceans (62% vs. 42%) and fin fish (78% vs. 58%) from the Gulf of Mexico compared to the inland group, while the inland group ate more fin fish not found in the Gulf of Mexico (62% vs. 33%). In the post-oil spill time period, both groups substantially reduced their consumption of sea food. On average, the coastal group ate ≥2 seafood meals per week, while the inland group ate ≤1 meal per week; these frequency patterns persisted in the post oil-spill period. Comparison of the estimated LOCs with contaminant levels detected in the seafood tested by the Food and Drug Administration and National Oceanic and Atmospheric Administration, post-oil spill, found that the levels of PAHs, arsenic, and DOSS in seafood were 1–2 orders of magnitude below the LOCs calculated in their study. Levels of methyl mercury (MeHg) in the seafood tested pre- and post- oil spill were higher than the estimated LOCs suggesting presence of higher levels of MeHg in seafood independent of the oil spill. Conclusion In sum, the study found higher than average seafood consumption among children along the Mobile coastal area when compared to the inland children and the National Health and Nutrition Examination Survey (NHANES) estimates. Risk characterization based on the LOCs indicated no increase in risk of exposure despite higher seafood consumption rates among the study population compared to the general population.

Schwichtenberg, F., Callies, U., Groll, N., Maßmann, S., Effects of chemical dispersants on oil spill drift paths in the German Bight-probabilistic assessment based on numerical ensemble simulations, *Geo-Marine Letters*, pp. 1-8, 2016

Schwichtenberg et al. (2016) model oil in the German Bight. They note that oil dispersed in the water column remains sheltered from wind forcing, so that an altered drift path is a key consequence of using chemical dispersants. In this study, ensemble simulations were conducted based on 7 years of simulated atmospheric and marine conditions, evaluating 2,190 hypothetical spills from each of 636 cells of a regular grid covering the inner German Bight (SE North Sea). Each simulation compares two idealized setups assuming either undispersed or fully dispersed oil. Differences are summarized in a spatial map of probabilities that chemical dispersant applications would help prevent oil pollution from entering intertidal coastal areas of the Wadden Sea. High probabilities of success overlap strongly with coastal regions between 10 m and 20 m water depth, where the use of chemical dispersants for oil spill response is a particularly contentious topic. The present study prepares the ground for a more detailed net environmental benefit analysis (NEBA) accounting also for toxic effects.

Scoma, A., Yakimov, M.M., Boon, N., Challenging oil bioremediation at deep-sea hydrostatic pressure, *Frontiers in Microbiology*, 7, AUG, pp. 1203, 2016a

Scoma et al. (2016a) note that many questions about the fate of petroleum-hydrocarbons within deep-sea environments remain unanswered, as well as the main constraints limiting bioremediation under increased hydrostatic pressures and low temperatures. The microbial pathways fueling oil bioassimilation are unclear, and the mild upregulation observed for beta-oxidation-related genes in both water and sediments contrasts with the high amount of alkanes present in the spilled oil. The fate of solid alkanes, hydrocarbon degradation rates and the reason why the most predominant hydrocarbonoclastic genera were not enriched at deep-sea despite being present at hydrocarbon seeps at the Gulf of Mexico have been largely overlooked. This mini-review aims at highlighting the missing information in the field, proposing a holistic approach where in situ and ex situ studies are integrated to reveal the principal mechanisms accounting for deep-sea oil bioremediation.

Scoma, A., Barbato, M., Borin, S., Daffonchio, D., Boon, N., An impaired metabolic response to hydrostatic pressure explains Alcanivorax borkumensis recorded distribution in the deep marine water column, *Scientific Reports*, 6, 31316, 2016

Scoma et al. (2016b) describe and study Alcanivorax borkumensis an ubiquitous model organism for hydrocarbonoclastic bacteria, which dominates polluted surface waters. Its negligible presence in oil-contaminated deep waters (as observed during the Deepwater Horizon accident) raises the hypothesis that it may lack adaptive mechanisms to hydrostatic pressure. The type strain SK2 was tested under 0.1, 5 and 10 MPa (corresponding to surface water, 500 and 1000 m depth, respectively). While 5 MPa essentially inactivated SK2, further increase to 10 MPa triggered some resistance mechanism, as indicated by higher total and intact cell numbers. Under 10 MPa, SK2 upregulated the synthetic pathway of the osmolyte ectoine, whose concentration increased from 0.45 to 4.71 fmoles cell^{-1}. Central biosynthetic pathways such as cell replication, glyoxylate and Krebs cycles, amino acids metabolism and fatty acids biosynthesis, but not β-oxidation, were upregulated or unaffected at 10 MPa, although total cell number was remarkably lower with respect to 0.1 MPa. Concomitantly, expression of more than 50% of SK2 genes was downregulated, including genes related to ATP generation, respiration and protein translation. Thus, A. borkumensis lacks proper adaptation to higher pressures but activates resistance mechanisms. These consist in poorly efficient biosynthetic rather than energy-yielding degradation-related pathways, and suggest that HP does represent a major driver for its distribution at deep-sea.

Seidel, M., Kleindienst, S., Dittmar, T., Joye, S.B., Medeiros, P.M., Biodegradation of crude oil and dispersants in deep seawater from the Gulf of Mexico: Insights from ultra-high resolution mass spectrometry, *Deep-Sea Research Part II: Topical Studies in Oceanography*, 129, pp. 108-118, 2016

Seidel et al. (2016) explore the biodegradation of oil, dispersant, dispersed oil or dispersed oil and nutrients at the molecular level using ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry following a laboratory experiment with Gulf deep water. Oil-derived molecular formulae exhibited a specific molecular fingerprint and were mainly observed in the mass range <300 Da. The relative abundance of heteroatom-containing (N, S, and P) compounds decreased over time in the oil-only treatments, indicating that they may have served as nutrients when oil-derived hydrocarbons were metabolized. Relative changes over time in the molecular composition were less pronounced in the dispersed oil treatments compared to the oil-only treatments, suggesting that dispersants affected the metabolic pathways of organic matter biodegradation. In particular, dispersant addition led to an increase of S-containing organic molecular formulae, likely derived from the surfactant di-octyl sulfosuccinate (DOSS). DOSS and several dispersant-derived metabolites (with and without S) were still detectable after six weeks of incubation, underscoring that they were not rapidly biodegraded under the experimental conditions. FT-ICR-MS fragmentation studies allowed tentatively assigning structures to several of these molecules, and the authors propose that they are degradation products of DOSS and other dispersant components. The present study suggests preferential degradation, transformation and enrichment of distinct dispersant molecules, highlighting the need to include these compounds when tracking Corexit-derived compounds in the environment.

Severin, T., Bacosa, H.P., Sato, A., Erdner, D.L., Dynamics of Heterocapsa sp. and the associated attached and free-living bacteria under the influence of dispersed and undispersed crude oil, *Letters in Applied Microbiology*, 63, 6, pp. 419-425, 2016

Severin et al. (2016) monitored the growth of Heterocapsa sp., an armoured dinoflagellate, exposed to crude oil, Corexit dispersant, or both. The effects on the biological complex formed by phytoplankton and their associated phytoplankton-attached (PA) and free-living (FL) bacteria are important considerations. However, associated bacteria can affect the physiology of phytoplankton and influence their stress responses. Growth of Heterocapsa sp. is unaffected by crude oil up to 25 ppm, a concentration similar to the lower range measured on Florida beaches after the Deepwater Horizon oil spill. The phytoplankton-attached bacteria community was resistant to exposure, whereas the FL community shifted towards oil degraders; both responses could contribute to Heterocapsa sp. oil resistance. The growth rate of Heterocapsa sp. decreased significantly only when exposed to dispersed oil at 25 ppm, indicating a synergistic effect of dispersant on oil toxicity in this organism.

Silva, C.S., de Oliveira, O.M.C., Moreira, I.T.A., Queiroz, A.F.S., de Almeida, M., Silva, J.V.L., da Silva Andrade, I.O., Potential application of oil-suspended particulate matter aggregates (OSA) on the remediation of reflective beaches impacted by petroleum: a mesocosm simulation, *Environmental Science and Pollution Research*, 13, 2015

Silva et al. (2015) study oil-suspended particulate matter aggregate (OSA) resulting from the interaction of droplets of dispersed oil in a water column and particulate matter. This structure reduces the adhesion of oil on solid surfaces, promotes dispersion, and may accelerate degradation processes. The effects of the addition of fine sediments (clay + silt) on the formation of OSA, their impact on the dispersion and degradation of the oil, and their potential use in recovering reflective sandy beaches were evaluated in a mesoscale simulation model. Two simulations were performed (21 days), in the absence and presence of fine sediments, with four units in each simulation using oil from the Recôncavo Basin. The results showed that the use of fine sediment increased the dispersion of the oil in the water column up to four times in relation to the sandy sediment. There was no evidence of the transport of hydrocarbons in bottom sediments associated with fine sediments that would have accelerated the dispersion and degradation rates of the oil. Most of the OSA that formed in this process remained in the water column, where the degradation processes were more effective. Over the 21 days of simulation, they observed a 40 % reduction on average of the levels of saturated hydrocarbons staining the surface oil.

Simpson, A.J., Mitchell, P.J., Masoom, H., Liaghati Mobarhan, Y., Adamo, A., Dicks, A.P., An oil spill in a tube: An accessible approach for teaching environmental NMR spectroscopy, *Journal of Chemical Education*, 92, 4, pp. 693-697, 2015

Simpson et al. describe a laboratory experiment introduces environmental NMR spectroscopy to upper-level undergraduate and graduate students in a simple and accessible manner. Students investigate the partitioning of crude oil components into water under various environmental conditions; assess the effects of agitation and dispersants on dissolution; and identify benzene, toluene, ethylbenzene, and xylene components through standard addition.

Singleton, B., Turner, J., Walter, L., Lathan, N., Thorpe, D., Ogbevoen, P., Daye, J., Alcorn, D., Wilson, S., Semien, J., Richard, T., Johnson, T., McCabe, K., Estrada, J.J., Galvez, F., Velasco, C., Reiss, K., Environmental stress in the Gulf of Mexico and its potential impact on public health, *Environmental Research*, 146, pp. 108-115, 2016

Singleton et al. (2016) employed portable airborne particulate matter samplers and a genetically engineered bacterial reporter system (umu-ChromoTest from EBPI) to determine levels of genotoxicity of air samples collected from highly contaminated areas of coastal Louisiana including Grand Isle, Port Fourchon, and Elmer's Island in the spring, summer and fall of 2011, 2012, 2013 and 2014. Air samples collected from a non-contaminated area, Sea Rim State Park, Texas, served as a control for background airborne genotoxic particles. In comparison to controls, air samples from the contaminated areas demonstrated highly significant increases in genotoxicity with the highest values registered during the month of July in 2011, 2013, and 2014, in all three locations. This seasonal trend was disrupted in 2012, when the highest genotoxicity values were detected in October, which correlated with hurricane Isaac landfall in late August of 2012, about five weeks before a routine collection of fall air samples. The data demonstrate: (i) high levels of air genotoxicity in the monitored areas over last four years post DWH oil spill; (ii) airborne particulate genotoxicity peaks in summers and correlates with high temperatures and high humidity; and (iii) this seasonal trend was disrupted by the hurricane Isaac landfall, which further supports the concept of a continuous negative impact of the oil spill in this region.

Sinski, J., Perry, H.M., Exner, J., Assessing Petroleum Contamination in Blue Crab *Callinectes sapidus* Megalopae Using Fluorescence Spectroscopy, *Journal of Shellfish Research*, 35, 2, pp. 507518, 2016

Sinski et al. (2016) assess the contamination of the DWH spill occurred in offshore waters considered important for blue crab larval development where there was high spatial and temporal overlap between blue crab larvae and the incident area. Exposure to contaminants may have occurred in both the offshore developmental phase and the nearshore settlement stage. Fluorescence spectroscopy techniques were developed to detect polycyclic aromatic hydrocarbon contamination in composite samples of tissue of 50 megalopae. Samples as low as 400 μl were analyzed allowing for detection of contaminants in very small sample sizes. Evidence of petroleum contamination was found in all megalopae harvested from the wild.

Skiba, Y.N., Parra-Guevara, D., Application of Adjoint Approach to Oil Spill Problems, *Environmental Modeling and Assessment*, pp. 1-17, 2016

Skiba and Para-Guevara (2016) describe a three-dimensional model for the dispersion of a quasi-passive substance (a pollutant or a nutrient) and its adjoint model are considered in a limited sea region.

Direct and adjoint estimates are used to get dual (equivalent) estimates of the mean concentration of the substance in important zones of the region. The role of dual estimates is illustrated with a few examples. They include such oil spill problems as the search of the most dangerous point of the oil tanker route, the oil dispersion with a climatic velocity, and the dependence of the oil concentration estimates on the oil spill rate. One more example is the application of optimal bioremediation strategy for cleaning areas polluted by oil. In this case, instead of oil, the model describes the dispersion of a nutrient released to marine environment. Balanced, unconditionally stable second-order finite-difference schemes based on the splitting method for the solution of the dispersion model and its adjoint are suggested. The main and adjoint difference schemes are compatible in the sense that at every fractional step of the splitting algorithm, the one-dimensional split operators of both schemes satisfy a discrete form of Lagrange identity. In the special unforced and non-dissipative case, each scheme has two conservation laws. Every split one-dimensional problem is solved by Thomas' factorization method.

Socolofsky, S.A., Adams, E.E., Boufadel, M.C., Aman, Z.M., Johansen, T., Konkel, W.J., Lindo, D., Madsen, M.N., North, E.W., Paris, C.B., Rasmussen, D., Reed, M., Rønningen, P., Sim, L.H., Uhrenholdt, T., Anderson, K.G., Cooper, C., Nedwed, T.J., Intercomparison of oil spill prediction models for accidental blowout scenarios with and without subsea chemical dispersant injection, *Marine Pollution Bulle*tin, 96, 02-Jan, pp. 110-126, 2015

Socolofsky et al. (2015) compare oil spill model predictions for a prototype subsea blowout with and without subsea injection of chemical dispersants in deep and shallow water, for high and low gas-oil ratio, and in weak to strong crossflows. Model results are compared for initial oil droplet size distribution, the nearfield plume, and the farfield Lagrangian particle tracking stage of hydrocarbon transport. For the conditions tested (a blowout with oil flow rate of 20,000 bbl/d, about 1/3 of the Deepwater Horizon), the models predict the volume median droplet diameter at the source to range from 0.3 to 6 mm without dispersant and 0.01 to 0.8 mm with dispersant. This reduced droplet size owing to reduced interfacial tension results in a one to two order of magnitude increase in the downstream displacement of the initial oil surfacing zone and may lead to a significant fraction of the spilled oil not reaching the sea surface.

Soloviev, A.V., Haus, B.K., McGauley, M.G., Dean, C.W., Ortiz-Suslow, D.G., Laxague, N.J.M., Özgökmen, T.M., Surface dynamics of crude and weathered oil in the presence of dispersants: Laboratory experiment and numerical simulation, *Journal of Geophysical Research: Oceans*, 121, 5, pp. 3502 -3516, 2016

Soloviev et al. conducted laboratory experiments focused on understanding the differences between the dynamics of crude and weathered oil spills and the effect of dispersants. After deposition on the still water surface, a drop of crude oil quickly spread into a thin slick; while at the same time, a drop of machine oil did not show significant evolution. Subsequent application of dispersant to the crude oil slick resulted in a quick contraction or fragmentation of the slick into narrow wedges and tiny drops. Notably, the slick of machine oil did not show significant change in size or topology after spraying dispersant. An advanced multi-phase, volume of fluid computational fluid dynamics model, incorporating capillary forces, was able to explain some of the features observed in the laboratory experiment. As a result of the laboratory and modeling experiments, the new interpretation of the effect of dispersant on the oil dispersion process including capillary effects has been proposed, which is expected to lead to improved oil spill models and response strategies.

Song, X., Zhang, B., Chen, B., Cai, Q., Use of Sesquiterpanes, Steranes, and Terpanes for Forensic Fingerprinting of Chemically Dispersed Oil, *Water, Air, and Soil Pollution*, 227, 8, 281,2016

Song et al. (2016) examined the stability and suitability of three groups of biomarkers, i.e., sesquiterpanes, steranes, and terpanes, for Chemically-Dispersed Oil (CDO) characterization in seawater after application of a representative chemical dispersant (Corexit 9500A). The results indicated that the suitability of sesquiterpanes as biomarkers for CDO identification was affected due to less number of stable diagnostic ratios and overlapped ranges of diagnostic ratios compared to other reference oils. On the contrary, most of the steranes and terpanes could still be applied as biomarkers for CDO characterization. All the selected diagnostic ratios of terpanes were suitable for identification of oil sources. By considering both the stability and suitability, the recommended ranking of biomarkers for CDO was terpanes > steranes > sesquiterpanes.

Spaulding, M.L., Isaji, T., Kim, Y.H., Selection of dispersion coefficients for use in Lagrangian spill transport models to preserve underlying flow dynamics and transport barriers, *39th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 22-34, 2016

Spaulding et al. (2016) developed a methodology that allows estimates to be made of the upper bound for dispersion coefficients used in a spill model to ensure that barriers to spill transport are identified and accurately accounted for in the spill model. The relative dispersion of uniformly seeded Lagrangian trajectories is computed for increasing values of the dispersion coefficient until the mixing barrier is no longer effective. The dispersion coefficient, at which the mixing barrier disappears, provides a dynamical estimate of the upper bound of its value. The method has been tested using a simulation of the circulation for a few day period during the Deepwater Horizon spill period using results from the SABGOM hydrodynamic model hindcast of surface and subsurface currents.

Starbird, K., Dailey, D., Walker, A.H., Leschine, T.M., Pavia, R., Bostrom, A., Social Media, Public Participation, and the 2010 BP Deepwater Horizon Oil Spill, *Human and Ecological Risk Assessment*, 21, 3, pp. 605-630, 2015

Starbird et al. (2015) examine how information about an oil spill, its impacts, and the use of dispersants to treat the oil, moved through social media and the surrounding Internet during the 2010 BP Deepwater Horizon oil spill. Using a collection of tweets captured during the spill, they employ a mixed-method approach including an in-depth qualitative analysis to examine the content of Twitter posts, the connections that Twitter users made with each other, and the links between Twitter content and the surrounding Internet. This article offers a range of findings to help practitioners and others understand how social media is used by a variety of different actors during a slow-moving, long-term, environmental disaster. They enumerate some of the most salient themes in the Twitter data, noting that concerns about health impacts were more likely to be communicated in tweets about dispersant use, than in the larger conversation. They describe the accounts and behaviors of highly retweeted Twitter users, noting how locals helped to shape the network and the conversation. Importantly, their results show the online crowd wanting to participate in and contribute to response efforts, a finding with implications for future oil spill response.

Størdal, I.F., Olsen, A.J., Jenssen, B.M., Netzer, R., Altin, D., Brakstad, O.G., Biotransformation of petroleum hydrocarbons and microbial communities in seawater with oil dispersions and copepod feces, *Marine Pollution Bulletin*, 101, 2, pp. 686-693, 2015a

Størdal et al. (2015a) studied biotransformation of components in crude oil dispersions in the presence of feces from marine copepods. Dispersed oil was incubated alone, with the addition of clean or oil-containing feces. They hypothesized that the feces would contribute nutrients to bacteria, and result in higher concentrations of oil-degrading bacteria. Presence of clean feces resulted in higher degradation of aromatic oil compounds, but lower degradation of n-alkanes. Presence of oil-containing feces resulted in higher degradation of n-alkanes. The effect of clean feces on aromatic compounds are suggested to be due to higher concentrations of nutrients in the seawater where aromatic degradation takes place, while the lower degradation of n-alkanes is suggested to be due to a preference by bacteria for feces over these compounds. Large aggregates were observed in oil dispersions with clean feces, which may cause sedimentation of un-weathered lipophilic oil compounds towards the seafloor if formed during oil spills.

Størdal, I.F., Olsen, A.J., Jenssen, B.M., Netzer, R., Hansen, B.H., Altin, D., Brakstad, O.G., Concentrations of viable oil-degrading microorganisms are increased in feces from Calanus finmarchicus feeding in petroleum oil dispersions, *Marine Pollution Bulletin*, 98, 02-Jan, pp. 69-77, 2015b

Størdal et al. (2015b) characterized feeding activity and microbial communities in feces from *Calanus finmarchicus* feeding in oil dispersions. Feeding activity was significantly reduced in oil dispersions. The microbial communities in clean and oil-containing copepod feces were dominated by Rhodobacteraceae family bacteria (Lesingera, Phaeobacter, Rugeria, and Sulfitobacter), which were suggested to be indigenous to copepod feces. The results also indicated that these bacteria were metabolizing oil compounds, as a significant increase in the concentrations of viable oil degrading microorganisms was observed in oil-containing feces. This study shows that bacteria in feces from copepods feeding in dilute oil dispersions have capacity for degradation of oil. Zooplankton may therefore contribute to weathering of oil by excreting feces with microbial communities already adapted to degradation of oil.

Studivan, M.S., Hatch, W.I., Mitchelmore, C.L., Responses of the soft coral Xenia elongata following acute exposure to a chemical dispersant, *SpringerPlus*, 4, 1, article no. 10, 2015

Studivan et al. (2015) studied dispersant exposure to corals. The aims of the study were: (1) to determine the extent of bleaching after acute 24 h and 72 h exposures of sublethal concentrations (0-50 ppm) of Corexit to the pulsing soft coral Xenia elongata and (2) to investigate a percent symbiont loss calculation using zooxanthellae density. The percent symbiont loss calculation was compared to a traditional metric of normalizing zooxanthellae density to soluble protein content. Percent symbiont loss was an effective measure of coral stress in acute Corexit exposures, while protein normalized zooxanthellae density was more variable. The bleaching data suggest a positive relationship between dispersant concentration and percent symbiont loss, culminating in excessive tissue necrosis and coral mortality within 72 h in high concentration exposures. Percent beaching ranged from 25% in 5 ppm exposures to 100% in 50 ppm exposures. Corexit also caused a significant decrease in pulse activity and relative oxygen saturation, possibly indicating a reduction in photosynthetic efficiency. This study and other similar research indicate that dispersant exposure is highly damaging to marine organisms, including ecologically important coral species.

Sun, J., Khelifa, A., Zhao, C., Zhao, D., Wang, Z., Laboratory investigation of oil-suspended particulate matter aggregation under different mixing conditions, *Science of the Total Environment*, 473-474, pp. 742-749, 2014

Sun et al. (2014) studied the effect of level and duration of mixing energy on OSA formation using the standard reference material 1941b and Arabian light crude oil. The results showed that dispersed small oil droplets increased with an increase of both the level and duration of mixing energy to form multi-droplet OSAs. The sizes of the dispersed droplets varied between 5 and 10 μm under different conditions studied. The maximum oil trapping efficiency increased from 23% to 33%, the oil to sediment ratio increased from 0.30 to 0.43 g oil/g sediment, and the required shaking time decreased from 2.3 to 1.1 h as the shaking rate increased from 2.0 to 2.3 Hz. Based on the size measurement results, a breakage effect on the formed OSAs and sediment flocs was confirmed under high mixing energy level.

Sun, J., Zhao, C.C., Xie, Z.J., Xu, G.B., Investigation of the effectiveness of a chemical dispersant under different mixing conditions, *Material Science and Environmental Engineering - Proceedings of the 3rd annual 2015 International Conference on Material Science and Environmental Engineering, ICMSEE 2015*, pp. 129-132, 2016

Sun et al. (2016) conducted a laboratory study to investigate the effectiveness of a widely used chemical dispersant in China under different mixing conditions, aiming to determine the optimum condition to apply this dispersant. In this study, TOPO crude oil and diesel oil were selected as the test oil. Filtered natural seawater, baffled flasks and a reciprocating shaker were used for the controlled experiment. The roles of oil type, and different environmental factors like mixing time, salinity and temperature in dispersant efficiency were studied systematically. The dispersant efficiency was evaluated based a settling time of 30 s and 10 min, respectively. The dispersed oil in the aqueous phase was characterized using an ultraviolet spectrophotometer. The results showed that oil type, the mixing energy applied, and temperature were key factors influencing the effectiveness of the dispersant. A better performance of the dispersant was observed when applying to TOPO crude oil. The highest effectiveness with a settling time of 30 s was 91%, and 65% with a settling time of 10 min. The dispersant efficiency increased with increase of the duration of the mixing energy applied, and also with the increase of temperature of the seawater from 10 to 30 °C.

Svalova, A., Abbott, G., Parker, N., Vane, C., Droplet size distribution of crude oil emulsions-stochastic differential equations and Bayesian modelling, *Petroleum Geostatistics*, pp. 318-322, 2015

Svalova et al. (2015) model oil droplet size growth as a stochastic process. Geometric Brownian motion (GBM) and its stochastic differential equations are used. Bayesian inference is introduced as a tool aiding in conditions of poor sample quality. The obtained model could predict emulsion separation indicated by a sufficiently large mean and standard deviation of the droplet growth process. It could be used for emulsions of different chemical compositions, including with added dispersants, allowing to characterise their impact on the WOE stability over time.

Svejkovsky, J., Hess, M., Muskat, J., Nedwed, T.J., McCall, J., Garcia, O., Characterization of surface oil thickness distribution patterns observed during the Deepwater Horizon (MC-252) oil spill with aerial and satellite remote sensing, *Marine Pollution Bulletin*, 110, 1, pp. 162-176, 2016

Svejkovsky et al. (2016) utilized very high resolution (≤ 5 m) aerial and satellite imagery acquired during the DWH spill to evaluate the shape, size and thickness of surface oil features. Results indicate that outside of the immediate spill source region, oil distributions did not encompass a broad, varied range of thicknesses. Instead, the oil separated into four primary, distinct characterizations: 1) invisible surface films detectable only with Synthetic Aperture Radar imaging because of the decreased surface backscatter, 2) thicker sheen and rainbow areas (< 0.005 mm), 3) large regional areas of relatively thin, “metallic appearance” films (0.005–0.08 mm), and 4) strands of thick, emulsified oil (> 1 mm) that were consistently hundreds of meters long but most commonly only 10–50 m wide. Where present within the slick footprint, each of the three distinct visible oil thickness classes maintained its shape characteristics both spatially (at different distances from the source and in different portions of the slick), and temporally (from mid-May through July 2010). The region over the source site tended to contain a more continuous range of oil thicknesses, however, their results indicate that the continuous injection of subsurface dispersants starting in late May significantly altered (lowered) that range.

Tansel, B., Arreaza, A., Tansel, D.Z., Lee, M., Decrease in osmotically driven water flux and transport through mangrove roots after oil spills in the presence and absence of dispersants, *Marine Pollution Bulletin*, 98, 02-Jan, pp. 34-39, 2015

Tansel et al. (2015) evaluated the effect of crude oil on water transport through mangroves roots in the presence and absence of dispersants. Water transport through the roots was evaluated experimentally using red mangrove root segments exposed to salt water contaminated with Louisiana crude oil for seven days in the presence and absence of Corexit 9500A (dispersant). Experimental observations were interpreted in view of the structural integrity and fouling phenomena observed on the epidermis and endodermis layers of the roots. The effects of oil on the radial water flux through the epidermis and endodermis were analyzed using a dual layer filtration model. Progression of fouling due to accumulation and penetration of the contaminants through the root layers were interpreted in relation to observed mangrove health (long and short term effects) reported in the literature.

Tarr, M.A., Zito, P., Overton, E.B., Olson, G.M., Adhikari, P.L., Reddy, C.M., Weathering of oil spilled in the marine environment, *Oceanography*, 29, 3, pp. 126-135, 2016

Tarr et al. (2016) review oil weathering noting that crude oil is a complex mixture of many thousands of mostly hydrocarbon and nitrogen-, sulfur-, and oxygen-containing compounds with molecular weights ranging from below 70 Da to well over 2,000 Da. When this complex mixture enters the environment from spills, ruptures, blowouts, or seeps, it undergoes a continuous series of compositional changes that result from a process known as weathering. Spills of petroleum involving human activity generally result in more rapid input of crude oil or refined products (diesel, gasoline, heavy fuel oil, and diluted bitumens) to the marine system than do natural processes and urban runoffs. The primary physicochemical processes involved in weathering include evaporation, dissolution, emulsification, dispersion, sedimentation/flocculation, microbial degradation, and photooxidation.

Taylor, E., Challenger, G., Rios, J., Morris, J., McCarthy, M.W., Brown, C., Dilbit crude oil weathering on brackish water: Meso-scale tests of behavior and spill countermeasures, *Proceedings of the 37th AMOP Technical Seminar on Environmental Contamination and Response*, pp. 317-337, 2014

Taylor et al. (2014) conducted weathering and countermeasures testing with Cold Lake Blend (CLB) and Access Western Blend (AWB) Dilbits from May 13 through May 26, 2013 at the Kinder Morgan/TransMountain Pipeline pump station in Gainford. Alberta. Based on visual observations, both dilbits exhibited properties that one would expect of a heavy, "conventional" crude oil. In no instance was any oil observed to have sunk. Densities increased as oil weathered approaching and, in some cases, exceeded 1000 kg/m^3. Viscosities increased rapidly with weathering exceeding 10,000 cP within 24 hours for both Dilbits exposed to moderate agitation. Visual observations of the surface of the oil in the various tanks showed that a crust formed as the oil weathered. Chemical analyses of the weathered oils and water column showed that concentrations of BTEX diminished rapidly although TPH values in the water column were variable and dependent on the degree of surface agitation. Countermeasures tested included dispersant application, burning, shoreline cleaners, and skimmers. Visual observations of the dispersant test revealed that Corexit 9500 was marginally effective on 6-hour weathered oil and not particularly effective for more weathered Dilbit. The test burn on 6-hour weathered oil was effective with a sustained burn and an estimated 70% oil combusted. Estimates show that approximately 50% of 24-hour weathered oil was burned, but only after sustained effort to ignite. The 72-hour weathered oil was not successfully ignited. Cleaning tests showed that removal of oil that had weathered for five days on water and then remained on tiles and exposed to air for four days was still effective when washing substrate treated with Corexit 9580. The time oil weathered on water before being placed on the tile was less important than the time the weathered oil was exposed to air. The three brush skimmers tested effectively recovered Dilbit throughout the oil weathering tests.

Temkin, A.M., Bowers, R.R., Magaletta, M.E., Holshouser, S., Maggi, A., Ciana, P., Guillette, L.J., Bowden, J.A., Kucklick, J.R., Baatz, J.E., Spyropoulos, D.D., Effects of crude oil/dispersant mixture and dispersant components on PPARγ activity in vitro and in vivo: Identification of dioctyl sodium sulfosuccinate (DOSS; CAS #577-11-7) as a probable obesogen, *Environmental Health Perspectives*, 124, 1, pp. 112-119, 2016

Temkin et al. (2016) investigated the environmental contamination resulting from the Deepwater Horizon (DWH) oil spill, including the use of the oil dispersant Corexit (a suspected obesogen) in remediation efforts, to determine whether obesogens were released into the environment during this incident. They also sought to improve the sensitivity of obesogen detection methods in order to guide post-toxicological chemical assessments. Peroxisome proliferator-activated receptor gamma (PPARγ) transactivation assays were used to identify putative obesogens. Solid-phase extraction (SPE) was used to sub-fractionate the water-accommodated fraction generated by mixing COREXIT, cell culture media, and DWH oil (CWAF). Liquid chromatography-mass spectrometry (LC-MS) was used to identify components of fractionated CWAF. PPAR response element (PPRE) activity was measured in PPRE-luciferase transgenic mice. Ligand-binding assays were used to quantitate ligand affinity. Murine 3T3-L1 preadipocytes were used to assess adipogenic induction. It was found that serum-free conditions greatly enhanced the sensitivity of PPARγ transactivation assays. CWAF and COREXIT had significant dose-dependent PPARγ transactivation activities. From SPE, the 50:50 water:ethanol volume fraction of CWAF contained this activity, and LC-MS indicated that major components of Corexit contribute to PPARγ transactivation in the CWAF. Molecular modeling predicted several components of Corexit might be PPARγ ligands. They classified dioctyl sodium sulfosuccinate (DOSS), a major component of Corexit, as a probable obesogen by PPARγ transactivation assays, PPAR-driven luciferase induction in vivo, PPARγ binding assays (affinity comparable to pioglitazone and arachidonic acid), and in vitro murine adipocyte differentiation. They concluded that DOSS is a putative obesogen worthy of further study, including epidemiological and clinical investigations into laxative prescriptions consisting of DOSS.

Tissier, F., Dussauze, M., Lefloch, N., Theron, M., Lemaire, P., Le Floch, S., Pichavant-Rafini, K., Effect of dispersed crude oil on cardiac function in seabass Dicentrarchus labrax, *Chemosphere*, 134, pp. 192-198, 2015

Tissier et al. (2015) assessed the impact of dispersed oil in *Dicentrarchus labrax*, a fish frequently used as an oil contamination indicator species. Fish were exposed for 48 h to (mechanically and chemically) dispersed oil and dispersant alone. The impact of these exposure conditions was assessed on cardiac function by measuring (i) the contraction strength, the contraction and the relaxation speeds (ii) the cardiac energy metabolism using respirometry on permeabilized cardiac fibers. Compared to control, the increase of polycyclic aromatic metabolites observed in the bile indicated oil contamination in the specimen fish. Following 48 h of oil exposure at realistic oil concentrations, alterations of cardiac performances were observed. A decrease in contraction strength, contraction and relaxation speeds was observed in the presence of oil without effect of dispersant on these three parameters. Looking at cardiac energy metabolism, dispersant alone decreases all the activity of the respiratory chain and increases the proton leak. From these results, it appears that the observed decrease in cardiac performance in fish exposed to oil was not linked to a decrease in energy availability.

Toyota, K., McNabb, N.A., Spyropoulos, D.D., Iguchi, T., Kohno, S., Toxic effects of chemical dispersant Corexit 9500 on water flea Daphnia magna, *Journal of Applied Toxicology*, 37, 2, pp. 201-206, 2017

The authors used the cladoceran crustacean, water flea *Daphnia magna* a well-established model species for freshwater toxicological tests, including detection of juvenile hormone-like activity in test compounds. They conducted laboratory experiments to investigate the acute and chronic toxicity of Corexit 9500 using D. magna. The acute toxicity test was conducted according to OECD TG202 and the 48 h EC50 was 1.31 ppm. The reproductive chronic toxicity test was performed following OECD TG211 ANNEX 7 and 21 days LOEC and NOEC values were 4.0 and 2.0 ppm, respectively. These results indicate that Corexit 9500 has toxic effects on daphnids, particularly during the neonatal developmental stage, whereas juvenile hormone-like activity was not identified of Corexit 9500 on daphnids. The authors suggest that application of this type of chemical dispersant may have serious impacts on freshwater ecosystems by disrupting the key food chain network.

van Eenennaam, J.S., Wei, Y., Grolle, K.C.F., Foekema, E.M., Murk, A.J., Oil spill dispersants induce formation of marine snow by phytoplankton-associated bacteria, *Marine Pollution Bulletin*, 104, 02-Jan, pp. 294-302, 2016

The researchers used two marine phytoplankton species (Dunaliella tertiolecta and Phaeodactylum tricornutum) to study marine snow formation. These phytoplankton produced EPS (Extracellular Polymeric Substances) or marine snow within days when exposed to the dispersant Corexit 9500. Phytoplankton-associated bacteria were shown to be responsible for the formation. The EPS consisted of proteins and to lesser extent polysaccharides. This study reveals an unexpected consequence of the presence of phytoplankton. This emphasizes the need to test the action of dispersants under realistic field conditions, which may seriously alter the fate of oil in the environment via increased marine snow formation.

Vander Zanden, H.B., Bolten, A.B., Tucker, A.D., Hart, K.M., Lamont, M.M., Fujisaki, I., Reich, K.J., Addison, D.S., Mansfield, K.L., Phillips, K.F., Pajuelo, M., Bjorndal, K.A., Biomarkers reveal sea turtles remained in oiled areas following the Deepwater Horizon oil spill, *Ecological Applications*, 26, 7, pp. 2145-2155, 2016

Vander Zanden et al. (2016) used long-term biological tissue records to provide pre-disaster data for a vulnerable marine organism, the sea turtle. Keratin samples from the carapace of loggerhead sea turtles record the foraging history for up to 18 years, allowing them to evaluate the effect of the oil spill on sea turtle foraging patterns. Samples were collected from 76 satellite-tracked adult loggerheads in 2011 and 2012, approximately one to two years after the spill. Of the 10 individuals that foraged in areas exposed to surface oil, none demonstrated significant changes in foraging patterns post spill. The observed long-term fidelity to foraging sites indicates that loggerheads in the northern Gulf of Mexico likely remained in established foraging sites, regardless of the introduction of oil and chemical dispersants. More research is needed to address potential long-term health consequences to turtles in this region.

Venosa, A.D., Anastas, P.T., Barron, M.G., Conmy, R.N., Greenberg, M.S., Wilson, G.J., Science-Based Decision Making on the Use of Dispersants in the Deepwater Horizon Oil Spill, *Oil Spill Remediation: Colloid Chemistry-Based Principles and Solutions*, pp. 1-17, 2014

Venosa et al. (2014) summarize the scientific perspectives in the aftermath of the DWH spill response. It includes an introduction, a brief history of dispersant use as a spill mitigation treatment, a summary of what is known about dispersion effectiveness from laboratory and wave tank research, a brief review of the toxicity of dispersants and dispersed oil, a review of monitoring technology developments in surface waters and in the deep sea, a discussion of fate and transport of the dispersed oil plume, and a summary of a comprehensive oil spill research strategy developed by EPA's Office of Research and

Development (ORD) to fill knowledge gaps. This research strategy has been provided to the Interagency Coordinating Committee on Oil Pollution Research (ICCOPR) as an aid in stimulating collaboration and cross-disciplinary research among the 13 federal agencies charged with developing and conducting advanced oil spill response technologies for remediating future oil spills.

Vibhute, A.M., Muvvala, V., Sureshan, K.M., A Sugar-Based Gelator for Marine Oil-Spill Recovery, *Angewandte Chemie - International Edition*, 55, 27, pp. 7782-7785, 2016

Vibhute et al. (2016) propose Phase-selective organogelators (PSOGs), molecules that can congeal oil selectively from oil–water mixtures. However, a major drawback lies in the mode of application of the PSOG to an oil spill spread over a large area. The proposed method of using carrier solvents is impractical for various reasons. Direct application of the PSOG as a solid, although it would be ideal, is unknown, presumably owing to poor dispersion of the solid through the oil. They have designed five cheap and easy-to-make glucose-derived PSOGs that disperse in the oil phase uniformly when applied as a fine powder. These gelators were shown to selectively congeal many oils, including crude oil, from oil–water mixtures to form stable gels, which is an essential property for efficient oil-spill recovery.

Vignier, J., Donaghy, L., Soudant, P., Chu, F.L.E., Morris, J.M., Carney, M.W., Lay, C., Krasnec, M., Robert, R., Volety, A.K., Impacts of Deepwater Horizon oil and associated dispersant on early development of the Eastern oyster Crassostrea virginica, *Marine Pollution Bulletin*, 100, 1, pp. 426-437, 2015

Vignier et al. (2015) evaluated the effects of exposing gametes and embryos of C. virginica to dispersant alone (Corexit), mechanically (HEWAF) and chemically dispersed (CEWAF) DWH oil. Fertilization success and the morphological development, growth, and survival of larvae were assessed. Gamete exposure reduced fertilization (HEWAF: EC_{20} 1 h = 1650 μg tPAH50 L^{-1}; CEWAF: EC_{20} 1 h = 19.4 μg tPAH50 L^{-1}; Corexit: EC_{20} 1 h = 6.9 mg L^{-1}). CEWAF and Corexit showed a similar toxicity on early life stages at equivalent nominal concentrations. Oysters exposed from gametes to CEWAF and Corexit experienced more deleterious effects than oysters exposed from embryos. Results suggest the presence of oil and dispersant during oyster spawning season may interfere with larval development and subsequent recruitment.

Vignier, J., Soudant, P., Chu, F.L.E., Morris, J.M., Carney, M.W., Lay, C.R., Krasnec, M.O., Robert, R., Volety, A.K., Lethal and sub-lethal effects of Deepwater Horizon slick oil and dispersant on oyster (Crassostrea virginica) larvae, *Marine Environmental Research*, 120, pp. 20-31, 2016

The researchers studied the effects of oil and dispersant on planktonic larval stages of the oyster, C. virginica (veliger (1-day), umbo (10-day) and pediveliger (14-day)) were tested in the laboratory. Exposures to HEWAF, CEWAF and dispersant were toxic to larvae impairing growth, settlement success and ultimately survival. Larval growth and settlement were reduced at concentrations of oil ranging from 1.7 to 106 μg/L for HEWAF and 1.1–35 μg/L for CEWAF, concentrations well within the range of water sampled during the DWH oil spill. Sublethal effects induced by oil and dispersant could have significant ecological implications on oyster populations.

Vignier, J., Volety, A.K., Rolton, A., Le Goïc, N., Chu, F.-L.E., Robert, R., Soudant, P., Sensitivity of eastern oyster (Crassostrea virginica) spermatozoa and oocytes to dispersed oil: Cellular responses and impacts on fertilization and embryogenesis, *Environmental Pollution*, 225, pp. 270-282, 2017

Vignier et al. (2017) evaluate the cellular effects of acute exposure of spermatozoa and oocytes to surface slick oil, dispersed mechanically (HEWAF) and chemically (CEWAF), using flow-cytometric (FCM) analyses, and (ii) determine whether the observed cellular effects relate to impairments of fertilization and embryogenesis of gametes exposed to the same concentrations of CEWAF and HEWAF. Following a 30-min exposure, the number of spermatozoa and their viability were reduced due to a physical action of oil droplets (HEWAF) and a toxic action of CEWAF respectively. Additionally, reactive oxygen species (ROS) production in exposed oocytes tended to increase with increasing oil concentrations suggesting that exposure to dispersed oil resulted in an oxidative stress. The decrease in fertilization success (1-h), larval survival (24-h) and increase in abnormalities (6-h and 24-h) may be partly related to altered cellular characteristics. FCM assays are a good predictor of sublethal effects especially on fertilization success. These data suggest that oil/dispersant are cytotoxic to gametes, which may affect negatively the reproduction success and early development of oysters.

Vikebø, F.B., Rønningen, P., Meier, S., Grøsvik, B.E., Lien, V.S., Dispersants have limited effects on exposure rates of oil spills on fish eggs and larvae in shelf seas, *Environmental Science and Technology*, 49, 10, pp. 6061-6069, 2015

Vikebø et al. (2015) used model simulations of a blow out of 4500 m^3 of crude oil per day (Statfjord light crude) for 30 days at three locations along the Norwegian coast. Eggs were modeled as released from nine different known spawning grounds, in the period from March 1st until the end of April, and all spawning products were followed for 90 days from the spill start at April first independent of time for spawning. They have modeled overlap between spawning products and oil concentrations giving a total polycyclic hydrocarbon (TPAH) concentration of more than 1.0 or 0.1 ppb (μg/l). At these orders of magnitude, they expect acute mortality or sublethal effects, respectively. In general, adding dispersants results in higher concentrations of TPAHs in a reduced volume of water compared to not adding dispersants. Also, the TPAHs are displaced deeper in the water column. Model simulations of the spill scenarios showed that addition of chemical dispersant in general moderately decreased the fraction of eggs and larvae that were exposed above the selected threshold values.

Volety, A., Boulais, M., Donaghy, L., Vignier, J., Loh, A.N., Soudant, P., Application of Flow Cytometry to Assess Deepwater Horizon Oil Toxicity on the Eastern Oyster Crassostrea virginica Spermatozoa, *Journal of Shellfish Research*, 35, 1, pp. 91-99, 2016

Volety et al. (2016) examined the impacts of chemically-enhanced water-accommodated fractions [CEWAF; 1.29-26.14 μg/l tPAH50 (a sum of 50 different polycyclic aromatic hydrocarbons)], high-energy water-accommodated fractions (HEWAF; 16.53-248.89 μg/l tPAH50), and dispersants (0.625-10 mg/l) on the cellular functions (viability, mitochondrial membrane potential (MMP), reactive oxygen species production (ROS), and acrosomal integrity) and resulting fertilization success of eastern oyster Crassostrea virginica spermatozoa. While viability of spermatozoa was not affected by CEWAF and HEWAF at concentrations tested, dispersant exposure caused significant decrease in viability at the highest concentration tested. Fertilization success as well as MMP and ROS production were significantly decreased upon exposure to CEWAF, HEWAF, and dispersants. Also, although not affected by HEWAF exposure, acrosomal integrity decreased upon exposure to CEWAF and dispersants at concentrations tested. The results of this study suggest that impaired fertilization and reduced viability observed after exposure to DWH oil spill contaminants may result, from alterations of cellular functions of spermatozoa and contribute to negative effects on oyster populations.

von Klitzing, R., Stehl, D., Pogrzeba, T., Schomäcker, R., Minullina, R., Panchal, A., Konnova, S., Fakhrullin, R., Koetz, J., Möhwald, H., Lvov, Y., Halloysites Stabilized Emulsions for Hydroformylation of Long Chain Olefins, *Advanced Materials Interfaces*, 4, 1, 1600435, 2017

The authors such halloysites as tubular alumosilicates, as inexpensive natural nanoparticles to form and stabilize oil–water emulsions. This stabilized emulsion was shown to enable efficient interfacial catalytic reactions. Yield, selectivity, and product separation can be tremendously enhanced, e.g., for the hydroformylation reaction of dodecene to tridecanal. In perspective, this type of formulation may be used for oil spill dispersions. The key elements of the described formulations are clay nanotubes (halloysites) which are highly anisometric, and can be filled by helper molecules.

Vonk, S.M., Hollander, D.J., Murk, A.J., Was the extreme and wide-spread marine oil-snow sedimentation and flocculent accumulation (MOSSFA) event during the Deepwater Horizon blow-out unique? *Marine Pollution Bulletin*, 100, 1, pp. 5-12, 2015

Vonk et al. (2015) note that during the Deepwater Horizon blowout, thick layers of oiled material were deposited on the deep seafloor. This large scale benthic concentration of oil is suggested to have occurred via the process of Marine Oil Snow Sedimentation and Flocculent Accumulation (MOSSFA). This meta-analysis investigates whether MOSSFA occurred in other large oil spills and identifies the main drivers of oil sedimentation. MOSSFA was found to have occurred during the IXTOC I blowout and possibly during the Santa Barbara blowout. Unfortunately, benthic effects were not sufficiently studied for the 52 spills reviewed. However, based on the current understanding of drivers involved, they conclude that MOSSFA and related benthic contamination may be widespread. They suggest to collect and analyze sediment cores at specific spill locations, as improved understanding of the MOSSFA process will allow better informed spill responses in the future, taking into account possible massive oil sedimentation and smothering of (deep) benthic ecosystems

Walker, A.H., Pavia, R., Bostrom, A., Leschine, T.M., Starbird, K., Communication Practices for Oil Spills: Stakeholder Engagement During Preparedness and Response, *Human and Ecological Risk Assessment*, 21, 3, pp. 667-690, 2015

Walker et al. (2015) review public engagement through both traditional and social media which was arguably much higher than in prior spills. The DWH response organization undertook a wide variety of activities to manage risks and communicate with both the general public and those directly affected, such as commercial fishers. However, these did not fully address widespread concerns about ecological and human health risks associated with dispersant use. Consequentially the DWH spill heightened awareness of persistent risk communication problems around oil spill response, and especially dispersant use. Oil spill risk research and experience suggests that institutional and operational factors inhibit engaging communities and stakeholders during oil spill preparedness and response, and that such engagement is essential for effective risk management. They review and assess current oil spill preparedness and response practices for community and stakeholder engagement, including related institutional and operational constraints. This assessment suggests five example risk management practices to improve and advance risk communications during oil spill preparedness and response activities.

Wang, A., Li, Y., Yang, X., Bao, M., Cheng, H., The enhanced stability and biodegradation of dispersed crude oil droplets by Xanthan Gum as an additive of chemical dispersant, *Marine Pollution Bulletin*, in press, 2016

Wang et al. (2016) used xanthan Gum (XG) as an additive in oil dispersant formulation to enhance the stability and biodegradation of dispersed crude oil droplets. When XG was used together with chemical dispersant 9500A, the dispersion effectiveness of crude oil in artificial sea water (ASW) and the oil droplet stability were both greatly enhanced. In the presence of XG, lower concentration of 9500A was needed to achieve the effective dispersion and stabilization. In addition to the enhancement of dispersion and stabilization, it was found that the biodegradation rate of crude oil by bacteria was dramatically enhanced when a mixture of 9500A and XG was used as a dispersant.

Wang, D., Adams, E.E., Intrusion dynamics of particle plumes in stratified water with weak crossflow: Application to deep ocean blowouts, *Journal of Geophysical Research: Oceans*, 121, 6, pp. 3820-3835, 2016

Wang and Adams (2016) carried out an experimental study of particle plumes in ambient stratification and a mild current. In an inverted framework, the results describe the fate of oil droplets released from a deep ocean blowout. A continuous stream of dense glass beads was released from a carriage towed in a salt-stratified tank. Non-dimensional particle slip velocity (UN) ranged from 0.1 to 1.9, and particles with UN $\leq$ 0.5 were observed to enter the intrusion layer. The spatial distributions of beads, collected on a bottom sled towed with the source, present a Gaussian distribution in the transverse direction and a skewed distribution in the along-current direction. Dimensions of the distributions increase with decreasing UN. The spreading relations can be used as input to far-field models describing subsequent transport of particles or, in an inverted framework, oil droplets. The average particle settling velocity, Uave, was found to exceed the individual particle slip velocity, Us, which is attributed to the initial plume velocity near the point of release. Additionally, smaller particles exhibit a “group” or “secondary plume” effect as they exit the intrusion as a swarm. The secondary effect becomes more prominent as UN decreases, and might help explain observations from the 2000 Deep Spill field experiment where oil was found to surface more rapidly than predicted based on Us. An analytical model predicting the particle deposition patterns was validated against experimental measurements, and used to estimate near-field oil transport under the Deepwater Horizon spill conditions, with/without chemical dispersants.

Wang, Q., Sun, B., Chu, Q., Yan, Z., Liu, H., Zhu, X., Yu, Y., T-test analysis of crude oil fingerprint impacted by dispersant, 2016 Xi'an Shiyou Daxue Xuebao (Ziran Kexue Ban)/*Journal of Xi'an Shiyou University, Natural Sciences Edition*, 31, 1, pp. 110-115, 2016

Wang et al. studied a mixture of Huabei crude oil with Haiou 4# dispersant, and their oil fingerprint identification based on diagnosis ratios. The study was finished by t-test analysis to study the effect of the dispersant on crude oil fingerprint. Firstly, GC-FID chromatograms of dispersant and 4 oil samples are compared, and the comparison result shows that the addition of dispersant will influence the chromatogram of crude oil. Secondly, the relative content of the n-alkanes (including pristane and phytane, Pr and Ph) in 4 oil samples was studied, and the result indicates that the addition of the dispersant will change the original relative content distribution of the n-alkanes' (including Pr and Ph) in crude oil, and the influence is obvious. Finally, each two samples are compared by t-test, and the results manifested that the fingerprints of 4 oil samples adding different amount of dispersant are different from each other, and they are different from the fingerprint of Huabei crude oil. The effects of the dispersant on C17/Pr and C18/Ph are the greatest, the influences of it on Pr/Ph and C17/C18 are greater, and its influences on (C23+C25+C27+C29)/(C24+C26+C28+C30) and (C19+C20)/(C19+C20+C21+C22) are the least. Therefore, the effect of dispersant on oil spill fingerprint identification needs to be considered.

Wang, Q.M., Sun, B., Yan, Z.Y., Chu, Q.D., Liu, H., Yu, Y., Comparison of analysis methods in oil added dispersant fingerprint identification, *Advances in Energy Science and Equipment Engineering - Proceedings of International Conference on Energy Equipment Science and Engineering, ICEESE 2015*, 1, pp. 497-500, 2015a

Wang et al. (2015) studied mixtures of Fuken-2 dispersant and Bohai crude oil. Repeatability limit and t-test methods were used in this paper to analyze the influence of dispersant in oil spill identification, and calculation results of the two were compared. The results of the former showed that, in addition to C17/Pr, influenced most easily when the dispersant content in oil was large, other diagnostic ratios were still suitable for the oil added dispersant identification. The results of the latter indicated that some fingerprints of oil added dispersant were inconsistent with the original ones, especially C17/Pr and C18/Ph, so the two were no longer suitable for the oil identification. Therefore, repeatability limit, compared with t-test method, is simple and could better avoid the interference of the dispersant.

Wang, Q.-M., Sun, B., Yan, Z.-Y., Zhu, X.-M., Liu, H., Xin, Y.-B., Stability research on the effect of oil spill dispersant I-separation characteristics of oil spill dispersant, *Open Petroleum Engineering Journal*, 8, pp. 90-92, 2015b

Wang et al. (2015b) studied the separation characteristics of an oil spill dispersant (OSD) and the oil were investigated, and the stability of the effect of the OSD was also studied. Firstly, the mixture of the oil and the OSD which have been poured into the seawater was thoroughly stirred, left to stand and observed. Later, the greatest separation degree with the oil and the final stability of the OSD was obtained through the analysis. Then, the stability of the combination between the oil and the OSD was studied under the conditions of no wave, intermittent wave and continuous wave. The study shows the OSD will gradually move away from the oil, which is influenced by the time and duration of the wave action.

Wang, Q.-M., Sun, B., Yan, Z.-Y., Zhu, X.-M., Liu, H., Xin, Y.-B., Stability research on the effect of oil spill dispersant II - Impact of wave intensity, *Open Petroleum Engineering Journal*, 8, pp. 93-96, 2015c

Wang et al. (2015c) conducted stability studies and the results show the OSD will gradually move away from the oil, and the quantity and speed of the removed OSD is influenced by the intensity and duration of the wave action. The stability mechanism of the OSD effect is proposed in this study.

White, H.K., Conmy, R.N., MacDonald, I.R., Reddy, C.M., Methods of oil detection in response to the Deepwater Horizon oil spill, *Oceanography*, 29, 3, PP. 76-87, 2016

White et al. (2016) review detection technologies during the DeepWater Horizon spill. Detecting oil in the northern Gulf of Mexico following the Deepwater Horizon oil spill presented unique challenges due to the spatial and temporal extent of the spill and the subsequent dilution of oil in the environment. Over time, physical, chemical, and biological processes altered the composition of the oil, further complicating its detection. Reservoir fluid, containing gas and oil, released from the Macondo well was detected in surface and subsurface environments. Oil monitoring during and after the spill required a variety of technologies, including nimble adaptation of techniques developed for non-oil-related applications. The oil detection technologies employed varied in sensitivity, selectivity, strategy, cost, usability, expertise of user, and reliability. Innovative technologies ranging from remote sensing to laboratory analytical techniques were employed and produced new information relevant to oil spill detection, including the chemical characterization, the dispersion effectiveness, and the detection limits of oil. The challenge remains to transfer these new technologies to oil spill responders so that detection of oil following a spill can be improved.

White, N.D., Godard-Codding, C., Webb, S.J., Bossart, G.D., Fair, P.A., Immunotoxic effects of in vitro exposure of dolphin lymphocytes to Louisiana sweet crude oil and Corexit, *Journal of Applied Toxicology*, 37, 6, pp. 676-682, 2017

White et al. (2016) examined the immunotoxicity of Louisiana sweet crude oil and the chemical dispersant Corexit using lymphocyte proliferation (LP) and natural killer cell (NK) assays as measures of impact on the adaptive (LP) and innate (NK) immune response in bottlenose dolphins. Study results show that both high-energy media-accommodated fractions (MAF) and chemically enhanced MAF (CEMAF) mixtures modulate immune function. Following exposure to Louisiana sweet crude, both B- and T-cell proliferation of white blood cells was increased for all exposure concentrations, compared to control; however, this increase was only significant for the 50% and 100% treatments. In contrast, exposure of white blood cells to the CEMAF mixture significantly decreased both T- and B-cell proliferation in the 25%, 50% and 100% treatments. NK cell activity was enhanced significantly by CEMAF mixtures for the 50% and 100% treatments. The immunosuppression of LP at environmentally relevant concentrations of oil and dispersant suggests that marine mammals may be unable to mount an adequate defense against xenobiotic threats following exposure to oil and dispersant, leaving them more susceptible to disease. In contrast, NK cell activity was significantly enhanced, which may increase an organism's tumor or viral surveillance ability by mounting an enhanced immune response.

Word, J.Q., Clark, J.R., Word, L.S., Comparison of the Acute Toxicity of Corexit 9500 and Household Cleaning Products, *Human and Ecological Risk Assessment*, 21, 3, pp. 707-725, 2015

Word et al. (2015) conducted laboratory tests by regulatory agencies to further evaluate and substantiate the existing aquatic toxicity of Corexit dispersants. To help put dispersant toxicity in context, two independent accredited labs were commissioned to conduct parallel studies that compared the acute toxicity of Corexit 9500 to common household cleaning agents. The results indicate that the acute toxicity of Corexit 9500 to marine aquatic organism is either within the median range or less toxic than the household cleaning agents tested. The median LC50 value for Corexit 9500 exposures to *Americamysis bahia* was 42.5 mg/L (four products were less toxic and four products were more toxic); whereas, the median LC50 value for Corexit 9500 exposures to *Menidia beryllina* was 73.1 mg/L (one product was less toxic and seven products were more toxic).

Wu, Y., Hannah, C.G., Thupaki, P., Mo, R., Law, B., Effects of rainfall on oil droplet size and the dispersion of spilled oil with application to Douglas Channel, British Columbia, Canada, *Marine Pollution Bulletin*, 114, 1, pp. 176-182, 2017

These researchers examined the influence of rain-induced turbulence on oil droplet size and dispersion of oil spills in Douglas Channel in British Columbia, using historic atmospheric data. The approach was to use a model largely based on Delvigne’s natural dispersion equation. Three types of oils: a light oil (Cold Lake Diluent - CLD), and two heavy oils (Cold Lake Blend - CLB and Access Western Blend - AWB) were tested. They found that the turbulent energy dissipation rate produced by rainfall is comparable to what is produced by wind-induced waves. With the use of chemical dispersants, the results indicate that a heavy rainfall can produce the maximum droplet size of 300 μm for light oil and 1000 μm for heavy oils, and it can disperse the light oil with fraction of 22–45% and the heavy oils of 8–13%, respectively. Heavy rainfall could be a factor for the fate of oil spills in Douglas Channel, especially for a spill of light oil and the use of chemical dispersants.

Xi, Y., Seyoum, H., Liu, M.-C., Role of SULT-mediated sulfation in the biotransformation of 2-butoxyethanol and sorbitan monolaurate: A study using zebrafish SULTs, *Aquatic Toxicology*, 177, pp. 19-21, 2016

Xi et al. (2016) noted that 2-Butoxyethanol and sorbitan monolaurate are major components of oil dispersants that are applied in large quantities to control oil spill in the aquatic environment. An important question is whether aquatic animals are equipped with mechanisms for the detoxification of these oil dispersant compounds. The current study aimed to examine whether zebrafish cytosolic sulfotransferases (SULTs) are capable of sulfating 2-butoxyethanol and sorbitan monolaurate. A systematic analysis of 18 zebrafish SULTs revealed that SULT3 ST1 showed the strongest sulfating activity toward 2-butoxyethanol, while SULT1 ST3 displayed the strongest sulfating activity toward sorbitan monolaurate. The pH-dependence of these two SULTs in mediating the sulfation of 2-butoxyethanol or sorbitan monolaurate was examined. Taken together, these results implied that SULT-mediated sulfation may function in the detoxification of these two oil dispersant compounds.

Xu, G., Cui, Z., Luan, X., Zheng, L., Genotoxicity evaluation of 6 chemical dispersants by luminescent bacteria test using Acinetobacter sp. RecA and fish exposure experiment using Oryzias melastigma, *Chinese Journal of Applied and Environmental Biology*, 23, 1, pp. 146-151, 2017

Xu et al. evaluated the genotoxicity of 6 unspecified chemical dispersants used for marine oil spills. They used luminescent bacteria test (LBT) based on Acinetobacter sp. RecA combined with fish exposure experiment based on marine medaka (Oryzias melastigma) to detect the genotoxicity of 6 chemical dispersants. In LBT, the 500 mg/L and 1 000 mg/L of chemical dispersant HLD-501 exhibited genotoxicity of 0.039 mg/L and 0.032 mg/L of mitomycin C (MMC), respectively. In addition, the DNA damage ratio of O. melastigma by the 6 chemical dispersants in the comet assay was in the order of concentrate type RS-II > concentrate type RS-I > conventional type HLD-501 > conventional type Fuken-2 > conventional type RS-I > conventional type Weipu. However, HLD-501 resulted in the most serious DNA damage (level 3), being the most genotoxic among the 6 dispersants. The result of these two methods for genotoxicity detection fitted well with each other.

Xue, J., Zheng, L., Lu, H., Guo, B., Wu, Y., Qiao, N., Yan, B., Treatment of oil polluted marine environment through multi-functional materials, *Journal of Chemical and Pharmaceutical Research*, 6, 5, pp. 1504-1509, 2014

Xue et al. (2014) introduce two types of multi-functional materials to deal with spill (e.g. adsorption materials and dispersants. In this paper, these two types materials were introduced and compared in detail.

Yan, B., Passow, U., Chanton, J.P., Nöthig, E.-M., Asper, V., Sweet, J., Pitiranggon, M., Diercks, A., Pak, D., Sustained deposition of contaminants from the Deepwater Horizon spill, *Proceedings of the National Academy of Sciences of the United States of America*, 113, 24, pp. E3332-E3340, 2016

Yan et al. (2016) showed that data from a deep sediment trap, deployed 7.4 km SW of the well between August 2010 and October 2011, revealed that the sinking of spill-associated substances, mediated by marine particles, especially phytoplankton, continued at least 5 months following the capping of the well. In August/September 2010, an exceptionally large diatom bloom sedimentation event coincided with elevated sinking rates of oil-derived hydrocarbons, black carbon, and two key components of drilling mud, barium and olefins. Barium remained in the water column for months and even entered pelagic food webs. Both saturated and polycyclic aromatic hydrocarbon source indicators corroborate a predominant contribution of crude oil to the sinking hydrocarbons. Co-sedimentation with diatoms accumulated contaminants that were dispersed in the water column and transported them downward, where they were concentrated into the upper centimeters of the seafloor, potentially leading to sustained impact on benthic ecosystems.

Yang, B., Xiong, D., Bioaccumulation and subacute toxicity of mechanically and chemically dispersed heavy fuel oil in sea urchin (Glyptocidaris crenulari) [Bioacumulación y toxicidad subaguda mecánica y químicamente dispersas de aceite combustible pesado de erizo de mar (Glyptocidaris crenulari)], *Scientia Marina*, 79, 4, pp. 497-504, 2015

Yang and Xiong (2015) analysed the hydrocarbon compositions of the mechanically dispersed water accommodated fraction (MDWAF) and the chemically dispersed water accommodated fraction (CDWAF) of No. 120 fuel oil, their bioaccumulation, and DNA damage related to oil exposure, using the sea urchin as a sentinel organism. The results show that the concentration of polycyclic aromatic hydrocarbon in the tissues of sea urchin exposed to the CDWAF is higher than that of those exposed to the MDWAF. The single cell gel electrophoresis assay results also indicated higher DNA damage from exposure to the CDWAF of oil. Thus, dispersants should be applied with caution in oil spill accidents.

Yang, D., Chen, B., Chamecki, M., Meneveau, C., Oil plumes and dispersion in Langmuir, upper-ocean turbulence: Large-eddy simulations and K-profile parameterization, *Journal of Geophysical Research C: Oceans*, 120, 7, pp. 4729-4759, 2015

Yang et al. (2015) note that once oil plumes such as those originating from underwater blowouts reach the ocean mixed layer (OML), their near-surface dispersion is influenced heavily by wind and wave-generated Langmuir turbulence. In this study, the complex oil spill dispersion process is modeled using large-eddy simulation (LES). The mean plume dispersion is characterized by performing statistical analysis of the resulting fields from the LES data. Although the instantaneous oil concentration exhibits high intermittency with complex spatial patterns such as Langmuir-induced striations, it is found that the time-averaged oil distribution can still be described quite well by smooth Gaussian-type plumes. LES results show that the competition between droplet rise velocity and vertical turbulent diffusion due to Langmuir turbulence is crucial in determining both the dilution rate and overall direction of transport of oil plumes in the OML. The smoothness of the mean plume makes it feasible to aim at modeling the oil dispersion using Reynolds-averaged type formulations, such as the K-profile parameterization (KPP) with sufficient vertical resolution to capture vertical profiles in the OML. Using LES data, they evaluate the eddy viscosity and eddy diffusivity following the KPP framework. They assess the performance of previous KPP models for pure shear turbulence and Langmuir turbulence by comparing them with the LES data. Based on the assessment a modified KPP model is proposed, which shows improved overall agreement with the LES results for both the eddy viscosity and the eddy diffusivity of the oil dispersion under a variety of flow conditions and droplet sizes.

Yednock, B.K., Sullivan, T.J., Neigel, J.E., De novo assembly of a transcriptome from juvenile blue crabs (Callinectes sapidus) following exposure to surrogate Macondo crude oil, *BMC Genomics*, 16, 1, p. 521, 2015

Yednock et al. (2015) sequenced transcriptomes from hepatopancreas and gill tissues of juvenile blue crabs after exposing them to a water-accommodated fraction of surrogate Macondo crude oil in the laboratory and compared them to transcriptomes from an unexposed control group. Illumina sequencing provided 42.5 million paired-end sequencing reads for the control group and 44.9 million paired-end reads for the treatment group. From these, 73,473 transcripts and 52,663 genes were assembled. Comparison of control and treatment transcriptomes revealed about 100 genes from each tissue type that were differentially expressed. However, a much larger number of transcripts, approximately 2000 from each tissue type, were differentially expressed. Several examples of alternatively spliced transcripts were verified by qPCR, some of which showed significantly different expression patterns. The combined transcriptome from all tissues and individuals was annotated to assign putative gene products to both major gene ontology categories as well as specific roles in responses to cold and heat, metabolism of xenobiotic compounds, defence, hypoxia, osmoregulation and ecdysis. Among the annotations for upregulated and alternatively-spliced genes were candidates for the metabolism of oil-derived compounds. It was found that previously, few genomic resources were available for blue crabs or related brachyuran crabs. The transcriptome sequences reported here represent a major new resource for research on the biology of blue crabs. These sequences can be used for studies of differential gene expression or as a source of genetic markers. Genes identified and annotated in this study include candidates for responses of the blue crab to xenobiotic compounds, which could serve as biomarkers for oil exposure. Changes in gene expression also suggest other physiological changes that may occur as the result of exposure to oil.

Yeudakimau, A.V., Perkins, C.R., Guerrera, G.M., Stuart, J.D., Provatas, A.A., QuEChERS sample preparation followed by ultra-performance liquid chromatography – tandem mass spectrometry for rapid screening of dioctyl sulfosuccinate sodium salt in avian egg tissue, I*nternational Journal of Environmental Analytical Chemistry*, 94, 12, pp. 1183-1198, 2014

Yeudakimau et al. (2014) developed a quantification method for the determination of dioctyl sulfosuccinate sodium salt (DOSS) in avian egg samples based on a QuEChERS extraction technique followed by UPLC-MS/MS analysis. DOSS is an anionic surfactant that is part of the Corexit 9500 dispersant. It was extensively used when the Deepwater Horizon rig exploded and a large amount of crude oil was released into the Gulf of Mexico. QuEChERS provided a simple, effective and time saving sample preparation method prior to analysis without reducing analytical sensitivity and became an excellent substitute to lengthy traditional extraction methods. Weak anionic exchange cleanup significantly reduced matrix effects and improved analyte sensitivity. Ultra-performance liquid chromatography provided an effective separation method, while MS/MS provided the necessary selectivity and increased sensitivity. Their method achieved baseline separation of DOSS, surrogate (sodium octyl sulfate – d17) and the internal standard (sodium dioctyl sulfate – d25), with limits of detection (LOD) and limits of quantitation (LOQ) for DOSS being 260 and 500 pg/mL, respectively. Quality control recoveries were 70.5 ± 7.3% for the laboratory control sample and 72.4 ± 4.9% (n = 3) for the matrix spike. The extraction efficiency was monitored by adding surrogate compound to every sample with recoveries of 104.6 ± 14.1 for SDS-d1 and 81.8 ± 6.8 for SOS-d17. Currently, limited peer reviewed scientific data are reported on the effects of oil dispersants on the environment. The analytical method for the determination of DOSS in avian egg matrix can be used to provide reliable data on the fate and effects of DOSS in biological systems.

Ylitalo, G.M., Collier, T.K., Anulacion, B.F., Juaire, K., Boyer, R.H., da Silva, D.A.M., Keene, J.L., Stacy, B.A., Determining oil and dispersant exposure in sea turtles from the northern Gulf of Mexico resulting from the Deepwater Horizon oil spill, *Endangered Species Research*, 33, 1, pp. 9-24, 2017

Ylitalo et al. (2017) collected substances from the skin of oiled and suspected oiled turtles and analyzed them for petroleum hydrocarbons to determine oiling status and oil sources. Tissue, gastroenteric and bile samples from a subset of visibly oiled and unoiled turtles that died during the spill in 2010 and in 2011 were analyzed for evidence of internal exposure and absorption of polycyclic aromatic hydrocarbons (PAHs) and the dispersant component dioctyl sodium sulfosuccinate (DOSS). The volume of external oil collected from sea turtles was sufficient to confirm the presence of petroleum on 61% of turtles, and oil from the DWH spill was identified as the source in 97% of those turtles in which conclusive comparison was possible. Visibly oiled turtles had higher concentrations of tissue PAH or biliary fluorescent PAH metabolites compared to those determined in unoiled animals. Findings in most of the unoiled turtles were suggestive of low-level PAH exposure from various sources that may represent background values for sea turtles from the northern GoM. DOSS levels were below the limit of quantitation in all samples analyzed except in an esophagus sample of a heavily oiled sea turtle. Overall, the results for petroleum or petroleum-derived compounds of both external and internal samples of sea turtles supported visual observations of oiling.

Zeinstra-Helfrich, M., Koops, W., Dijkstra, K., Murk, A.J., Quantification of the effect of oil layer thickness on entrainment of surface oil, *Marine Pollution Bulletin*, 96, 02-Jan, pp. 401-409, 2015a

Zeinstra-Helfrich et al. quantified the effect of oil layer thickness on entrainment and dispersion of oil into seawater, using a plunging jet with a camera system. In contrast to what is generally assumed, they revealed that for the low viscosity "surrogate MC252 oil" they used, entrainment rate is directly proportional to layer thickness. Furthermore, the volume of stably suspended small oil droplets increases with energy input (plunge height) and is mostly proportional to layer thickness. Oil pre-treated with dispersants (dispersant-oil ratio ranges from 1:50 to 1:300) is largely entrained in such large amounts of small droplets that quantification was impossible with the camera system. Very low interfacial tension causes entrainment by even minor secondary surface disturbances. Their results indicate that the effect of oil layer thickness should be included in oil entrainment and dispersion modelling.

Zeinstra-Helfrich, M., Koops, W., Murk, A.J., The NET effect of dispersants - A critical review of testing and modelling of surface oil dispersion, *Marine Pollution Bulletin*, 100, 1, pp. 102-111, 2015b

Zeinstra-Helfrich et al. (2015b) studied how natural, chemical and mechanical dispersion could be quantified in oil spill models. For each step in the dispersion process, they review available experimental data in order to identify overall trends and propose an algorithm or calculation method. Additionally, the conditions for successful mechanical and chemical dispersion are defined. Two commonly identified key parameters in surface oil dispersion are: oil properties (viscosity and presence of dispersants) and mixing energy (often wind speed). Strikingly, these parameters play a different role in several of the dispersion sub-processes. This may explain difficulties in simply relating overall dispersion effectiveness to the individual parameters.

Zeinstra-Helfrich, M., Koops, W., Murk, A.J., How oil properties and layer thickness determine the entrainment of spilled surface oil, *Marine Pollution Bulletin*, 110,1, pp. 184-193, 2016

Zeinstra-Helfrich et al. (2016) investigated entrainment rate and initial droplet size distribution for seven different oil grades using a plunging jet apparatus with coupled camera equipment and subsequent image analysis. They found that amount of oil entrained is proportional to layer thickness and largely independent of oil properties: A dispersant dose of 1:200 did not result in a significantly different entrainment rate compared to no dispersants. Oil viscosity had a minor to no influence on entrainment rate, until a certain threshold above which entrainment was impeded. The mean droplet size scales with the modified Weber number as described by Johansen. The obtained results can help improve dispersion algorithms in oil spill fate and transport models, to aid making an informed decision about application of dispersants.

Zhang, Q.-Q., Cai, B.-X., Xu, W.-J., Gang, H.-Z., Liu, J.-F., Yang, S.-Z., Mu, B.-Z., Novel zwitterionic surfactant derived from castor oil and its performance evaluation for oil recovery, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 483, pp. 87-95, 2015

Zhang et al. (2015) report on a novel zwitterionic surfactant derived from castor oil and its performance for oil recovery. The surface tension of the surfactant solution reached 30.7 mN/m at its critical micelle concentration value of 7.08×10^{-6}mol/L. The interfacial tension between crude oil and water could be reduced to ultra-low value as 5.4×10^{-3}mN/m at a low dosage of 0.010 g/L in aqueous solution with the absence of any extra alkali. When used as dispersant, the dispersion effectiveness of crude oil was 64.69%. Meanwhile, the bio-based surfactant demonstrated strong electrolyte tolerance, temperature resistance and thermostability, better wetting and foaming performance.

Zhang, Z., Avij, P., Perkins, M.J., Liyana-Arachchi, T.P., Field, J.A., Valsaraj, K.T., Hung, F.R., Combined Experimental and Molecular Simulation Investigation of the Individual Effects of Corexit Surfactants on the aerosolization of Oil Spill Matter, *Journal of Physical Chemistry A*, 120, 30, pp. 6048-6058, 2016

Zhang et al. (2016) carried out laboratory aerosolization experiments and classical molecular dynamics (MD) simulations, with the objective of investigating the individual effects of the two Corexit surfactants Span 80 (non-ionic) and dioctyl sodium sulfosuccinate (DOSS, ionic), on the aerosolization of oil spill material to the atmosphere. Their simulation results show that Span 80, DOSS, and the oil alkanes n-pentadecane (C15) and n-triacontane (C30) exhibit deep free energy minima at the air/seawater interface. C15 and C30 exhibit deeper free energy minima at the interface when Span 80 is present, as compared to the situation when DOSS or no surfactants are at the interface. These results suggest that Span 80 makes these oil hydrocarbons more likely to be adsorbed at the surface of seawater droplets and carried out to the atmosphere, relative to DOSS or to the situation where no surfactants are present. These simulation trends are in qualitative agreement with their experimental observations in a bubble-column setup, where larger amounts of oil hydrocarbons are ejected when Span 80 is mixed with oil and injected into the column, as compared to when DOSS is used. Their simulations also indicate that Span 80 has a larger thermodynamic incentive than DOSS to move from the seawater phase and into the air/seawater interface. This observation is also in qualitative agreement with their experimental measurements, which indicate that Span 80 is ejected in larger quantities than DOSS. The simulations also suggest that DOSS predominantly adopts a perpendicular orientation with respect to the air/seawater interface at a dispersant to oil ratio (DOR) of 1:20, but has a slight preference to lie parallel to the interfaces at a DOR = 1:5; in both cases, DOSS molecules have their tails wide open and stretched. In contrast, Span 80 has a slight preference to align parallel to the interfaces with a coiled conformation at both DOR values.

Zhao, L., Boufadel, M.C., Adams, E., Socolofsky, S.A., King, T., Lee, K., Nedwed, T., Simulation of scenarios of oil droplet formation from the Deepwater Horizon blowout, *Marine Pollution Bulletin*,101, 1, pp. 304-319, 2015

Zhao et al. (2015) considered hypothetical scenarios of releases that explore the realistic parameter space using a thoroughly calibrated DSD model, VDROP-J, and they attempted to provide bounds on the range of droplet sizes from the DWH blowout within 200 m of the wellhead. The scenarios include conditions without and with the presence of dispersants, different dispersant treatment efficiencies, live oil and dead oil properties, and varying oil flow rate, gas flow rate, and orifice diameter. The results, especially for dispersant-treated oil, are very different from recent modeling studies in the literature.

Zhao, L., Shaffer, F., Robinson, B., King, T., D'Ambrose, C., Pan, Z., Gao, F., Miller, R.S., Conmy, R.N., Boufadel, M.C.,Underwater oil jet: Hydrodynamics and droplet size distribution, *Chemical Engineering Journal*, 299, pp. 292-303, 2016a

Zhao et al. (2016a) conducted a large-scale experiment of underwater oil release of 6.3 L/s through a 25.4 mm (one inch) horizontal pipe. Detailed measurements of plume trajectory, velocity, oil droplet size distribution, and oil holdup were obtained. The obtained experimental data were used for the validation of the models JETLAG and VDROP-J. Key findings include: (1) formation of two plumes, one due to momentum and subsequently plume buoyancy, and another due mostly to the buoyancy of individual oil droplets that separate upward from the first plume; (2) modeling results indicated that the traditional miscible plume models matched the momentum and buoyancy plume, but were not able to simulate the upward motion plume induced by individual oil droplets; (3) high resolution images in the jet primary breakup region showed the formation of ligaments and drops in a process known as "primary breakup". These threads re-entered the plume to re-break in a process known as "secondary breakup"; (4) the plume velocity was highly heterogeneous with regions of high velocity surrounded by stagnant regions for various durations. The results from this study revealed that the primary breakup is a key factor for quantifying the droplet size distribution which plays a crucial role in determining the ultimate fate and transport of the released oil in the marine environment. The observed spatial heterogeneity in the oil plume implies that the effectiveness of applied dispersants may vary greatly when applying directly in the discharged oil flow.

Zhao, L., Wang, B., Armenante, P.M., Conmy, R., Boufadel, M.C., Characterization of turbulent properties in the EPA baffled flask for dispersion effectiveness testing, *Journal of Environmental Engineering (United States)*,142, pp. 1, 2016b

Zhao et al. (2016b) investigated the mixing energy in the baffled flask. Particle image velocimetry (PIV) was used to measure the water velocity in the flask placed at an orbital shaker that was rotated at seven rotation speeds: 100, 125, 150, 160, 170, 200, and 250 rpm. Two-dimensional velocity fields in large and small vertical cross sections of the flask for each rotation speed were obtained. The one-dimensional (1D) energy spectra indicates the existence of inertial subrange. The estimated average energy dissipation rates were in the range 7.65×10^{-3} to 4 W/kg for rotation speeds of ω=100-250 rpm, of which it is larger than the one estimated by prior studies using single-point velocity measurement techniques for ω=100 and 200 rpm. Factors such as instruments used, velocity components measured, and different analysis methods could contribute to the discrepancies in the results. The Kolmogorov scale estimated in this study for all seven rotation speeds approached the size of oil droplets observed at sea, which is 50-400 μm. The average energy dissipation rate, e and Kolmogorov microscale, n, in the flasks were correlated to the rotation speed, and it was found that e¯$=9.0\times10^{-5}$ Exp(0.043ω) with $R^2=0.97$ and n¯=1,463 Exp(-0.015ω) with $R^2=0.98$.

Zhao, X., Gong, Y., O'Reilly, S.E., Zhao, D., Effects of oil dispersant on solubilization, sorption and desorption of polycyclic aromatic hydrocarbons in sediment-seawater systems, *Marine Pollution Bulletin*, 92, 02-Jan, pp. 160-169, 2015

Zhao et al. (2015) investigated effects of a prototype oil dispersant on solubilization, sorption and desorption of three model PAHs in sediment-seawater systems. Increasing dispersant dosage linearly enhanced solubility for all PAHs. Conversely, the dispersant enhanced the sediment uptake of the PAHs, and induced significant desorption hysteresis. Such contrasting effects (ad-solubilization vs. solubilization) of dispersant were found dependent of the dispersant concentration and PAH hydrophobicity. The dual-mode models adequately simulated the sorption kinetics and isotherms, and quantified dispersant-enhanced PAH uptake. Sorption of naphthalene and 1-methylnaphthalene by sediment positively correlated with uptake of the dispersant, while sorption of pyrene dropped sharply when the dispersant exceeded its critical micelle concentration (CMC). The Deepwater conditions diminished the dispersant effects on solubilization, but enhanced uptake of the PAHs, albeit sorption of the dispersant was lowered.

Zhao, X., Liu, W., Fu, J., Cai, Z., O'Reilly, S.E., Zhao, D., Dispersion, sorption and photodegradation of petroleum hydrocarbons in dispersant-seawater-sediment systems, *Marine Pollution Bulletin*, 109,1, pp. 526-538, 2016

The authors examined effects of model oil dispersants on dispersion, sorption and photodegradation of petroleum hydrocarbons in simulated marine and sediment systems. Three dispersants (Corexit 9500A, Corexit 9527A and SPC 1000) were used to prepare dispersed water accommodated oil (DWAO). While higher doses of dispersants dispersed more n-alkanes and PAHs, Corexit 9500A preferentially dispersed C11–C20 n-alkanes, whereas Corexit 9527A was more favorable for smaller alkanes (C10–C16), and SPC 1000 for C12–C28 n-alkanes. Sorption of petroleum hydrocarbons on sediment was proportional to TPH types/fractions in the DWAOs. Addition of 18 mg/L of Corexit 9500A increased sediment uptake of 2–3 ring PAHs, while higher dispersant doses reduced the uptake. Both dispersed n-alkanes and PAHs were susceptible to photodegradation under simulated sunlight. For PAHs, both photodegradation and photo-enhanced alkylation were concurrently taking place.

Zhu, H., You, J., Zhao, H., Underwater spreading and surface drifting of oil spilled from a submarine pipeline under the combined action of wave and current, *Applied Ocean Research*, 64, pp. 217-235, 2017

Zhu et al. carried out numerical investigation on the underwater spread and surface drift of oil spilled from a submarine pipeline under the combined action of wave and current was carried out to examine the effects of physical ocean environment, leaking flux and spilled oil density and viscosity. Reynolds-Averaged-Navier-Stokes (RANS) equations, realizable k-ε turbulence model and volume of fluid (VOF) model are employed to describe the multiphase flow, and velocity-boundary wave-making technique combined with the sponge layer damping absorber technique realizes the numerical wave flume. Oil spill experiments were conducted to validate the numerical model. The calculation results indicate that compared with the environmental conditions of still water, only current and only wave, a larger scope of underwater spreading and relatively slower rising rate and relatively faster drifting rate of oil droplets are observed under the combined action of wave and current. The leaking flux affects the floating time and dispersion concentration, while the ocean environment affects the horizontal migration and surface drifting. Under the specific conditions of present work, oil density has obvious effect on the underwater spread but limited effect on the surface drifting, while oil viscosity has little effect on both the two processes.

Zhuang, X., Pi, Y., Bao, M., Li, Y., Zheng, X., The physical-biological processes of petroleum hydrocarbons in seawater/sediments after an oil spill, *RSC Advances*, 5, 120, pp. 98990-98998, 2015

Zhuang et al. (2015) investigated the adsorption and desorption behaviors of dissolved petroleum hydrocarbons (DPHs) in a seawater-sediment system. Tidal flat sediment was used as the adsorbent, and crude oil was used as the adsorbate. The processes of adsorption and desorption at low concentration (<14.3 mg L-1) were described by the first-order kinetics model. The rate of desorption was slower than that of adsorption, and about 49% of the DPHs remained on the sediment. Therefore, the potential risk of pollution would exist for a long time. The adsorption isotherms could be better fitted to the linear isotherm model than the Freundlich and Langmuir models. The adsorption process is a physical adsorption, because ΔH was 39.0 kJ mol-1 which is less than 42.0 kJ mol-1. The change in n-alkanes in the process was more obvious than the aromatics; the weathering loss rate was 25.56%, the emulsification loss rate of the dispersant was 0.65% and the microbial degradation rate was 15.46%. The results showed the degradation processes of petroleum hydrocarbons in tidal flats.

Summaries from Previous Literature Reviews

2002

2008

2014

2002 Literature Review
Summary and Issues

Overall

The literature on oil spill dispersants since 1997 is extensive, consisting of approximately 125 papers. The effectiveness of dispersants continues to be a major issue. Tests results with Alaskan crude oils show wide disparities in the effectiveness of dispersants. New results for moderate-energy apparatus show effectiveness values of 5 to 15% for Alaska North Slope at salinities of about 20^o/oo and temperatures of about 10^{o}C. High-energy tests such as the MNS, IFP, and EXDET show much higher values, but at higher temperatures and salinities.

There are a number of new toxicity studies. Many of these show that the acute toxicity of chemically dispersed oil and physically dispersed oil is different for different species. In most of the cases, the chemically dispersed oil is somewhat more toxic than the physically dispersed oil. Studies of the food chain show that dispersed oil is more likely to result in the passage of naphthalene through the food chain. Similarly, body burdens of PAHs vary depending on species and the presence of chemically or physically dispersed oil.

There is little new in operational matters regarding dispersants. The finding that Corexit 9500 is much less effective on thick oil slicks when applied diluted with water than when applied neat is, however, a significant one.

Efficacy of Dispersants in Alaskan Waters

The efficacy of dispersants in Alaskan waters remains an unknown. Recent literature shows that the effectiveness of Corexit 9527 on Alaska North Slope, as measured in laboratory tests at the same temperatures and salinities as found in Prince William Sound, would range from 5 to 10%. Tests at regular temperatures for range show effectiveness for Corexit 9527 range from 16 to 57% for Prudhoe Bay or Alaska North Slope crude oils. High-energy tests show percentages above this mark. Some new data questions the high-energy test results, indicating that in the field, results even lower than the moderate-energy tests are more likely.

Dispersants Stockpiled in Alaska

The primary dispersant stockpiled in Alaska is Corexit 9527. Although much of the current thinking is that Corexit 9500 would yield higher effectiveness results, laboratory tests show that this is not necessarily so. There are about equal numbers of laboratory results that show Corexit 9527 is more effective on Alaskan crudes and those that show Corexit 9500 is better. It should be noted that the same surfactant package is included in the formulation of both dispersants.

Operational Descriptions of Dispersant Use

There are no new descriptions in the literature of operations directly relevant to dispersant use in Alaska. There have been three small applications of dispersant in the Gulf of Mexico, however, oil is highly dispersible and the water temperatures much higher in the Gulf of Mexico. There are no cold water dispersant applications in the literature. Only one dispersant application other than those in the Gulf was noted in the world, that of the *Sea Empress* case in Britain. In this case, dispersants were applied from DC-3 and Hercules aircraft over a part of the slick. Mass balance calculations indicated a loss of oil, although there was extensive coastal oiling at this incident.

A significant new finding was that Corexit 9500 was significantly less effective when applied diluted with water than when applied neat.

Dispersants Not Stockpiled in Alaska

The only potentially useful dispersant not stockpiled extensively in Alaska is Corexit 9500. As already noted, there is variable data on the difference in effectiveness of Corexit 9527 and 9500 on Alaskan crude oils.

What Impacts Will Non-dispersed Remnants Have?

Extensive studies on the behaviour and fate of non-dispersed remnants of oil have not been conducted. There is no reason to believe that the effects of these remnants on the environment would be much different than the oil by itself. As reviewed in this report, there is extensive literature in recent years that shows that dispersed oil and untreated oil generally have similar effects on species, with this being somewhat species-dependent. For some species, the added dispersant may present a problem, whereas for others, it may present less of a problem. It is suspected that undispersed oil treated with dispersant is less adhesive, which is beneficial for shorelines, but not for physical recovery. No definitive tests have been conducted on this.

Policies in Other Parts of the World

Policies concerning dispersants in other parts of the world have not changed significantly since the last report. In Europe, only Britain uses dispersants extensively, although they may be used in Norway and France. No documented use of dispersants has been found in any European country except for the *Sea Empress* case noted throughout this report. The Baltic countries do not use dispersants and laws against their use are found nationally and internationally in the HELCOM treaties. In North America, several states in the U.S. have moved to allow dispersant use, but dispersants have only been used three times, all of them in the Gulf of Mexico.

2008 Literature Summary

Overall

The literature on oil spill dispersants between 1997 and 2008 is extensive, consisting of more than 430 papers. The prime motivation for using dispersants is to reduce the impact of oil on shorelines. To accomplish this, the dispersant application must be highly successful and effectiveness high. As some oil would come ashore, there is much discussion on what effectiveness is required to significantly reduce the shoreline impact. A major issue that remains is the actual effectiveness during spills so that these values can be used in estimates for assessment and models.

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

The third motivation for using dispersants is to promote the biodegradation of oil in the water column. The effect of dispersants on biodegradation is still a matter of discussion. There are a number of contradictory papers stating that dispersants inhibit biodegradation others indicate that dispersants have little effect on biodegradation. The most recent papers, however, confirm that inhibition is a matter of the surfactant in the dispersant itself and the factors of environmental conditions. What is very clear at this time is that the surfactants in some of the current dispersant formulations can either inhibit or leave biodegradation unaffected. In recent studies it was never shown that dispersants clearly enhanced biodegradation. Further, there are issues about the biodegradability of the surfactant themselves and this fact can confound many tests of dispersed oil biodegradation. As the NAS committee (2006) pointed out that older tests that may have shown enhanced biodegradation with dispersants, were flawed in that they were conducted under high nutrient conditions and over times that were not representative of oceanic conditions. An important issue that rarely is discussed is that oil-degrading bacteria, largely live on the water surface, where they would feed on similar natural hydrocarbons in the absence of spills. Another serious question is that of time scale. Biodegradation takes place over weeks, months and years compared to dispersion half lives of 12 to 36 hours.

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

Effectiveness Testing Overall

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

Effectiveness issues are confounded by the fact that various tests show highly different results depending on how they are constructed and operated. Detailed scientific examination of most of these shows 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. It has been noted that many of the current tests may be too energetic as they yield results well above that obtained in older field tests.

Tank Testing

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

Analytical Methods for Effectiveness

Analytical means continues to be a major concern for effectiveness testing. It is very clear that only careful GC/MS techniques produce a true answer. There are few analytical methods that can be used outdoors or in field situations. Very early in the field testing program, fluorometers were used. Studies then 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 invalid colorimetric method also continues to be used in a few cases for laboratory tests.

Toxicity of Dispersed Oil and Dispersants

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

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

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

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

Biodegradation of Oil Treated by Dispersants

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

Spill-of-Opportunity Research

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

Monitoring Dispersant Applications

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

Dispersant Use in Recent Times

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

Interaction with Sediment Particles

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

Stability of Dispersions and Resurfacing with Time

Oil spill dispersions are not stable and dispersed oil will 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.

Efficacy of Dispersants in Alaskan Waters

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

Weather and Application of Dispersants in Alaska

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

Dispersants Stockpiled in Alaska

The primary dispersant stockpiled in Alaska is Corexit 9527. Although much of the current thinking is that Corexit 9500 would yield higher effectiveness results, laboratory tests show that this is not necessarily so. There are about equal numbers of laboratory results that show that Corexit 9527 is more effective on Alaskan crudes and those that show that Corexit 9500 is better. It should be noted that the same surfactant package is included in the formulation of both dispersants.

Fate of Dispersed Oil

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

Application Technology and Issues

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

Correlation of Oil Properties with Effectiveness

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

Recommendations for Further Research

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

2014 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 shows 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 areas such as in Prince William Sound.

Subsea Application and Subsea Behavior

During the Deepwater Horizon spill extensive use of dispersant was made subsea. 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 certainly is needed.

Recommendations for Further Research

The author of this report has given his own recommendations.