Review of Literature on Oil Spill Dispersants:

2021-2023

for

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Anchorage, Alaska

by

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Disclaimer: The opinions expressed in this PWSRCAC-commissioned report are not necessarily those of PWSRCAC

January 2023

Foreword

This is a summary report on dispersants and dispersant research. This is an update to the previous detailed summary which was prepared in 2021. Emphasis in this summary report is placed on aspects that relate to Alaska and Prince William Sound. This summary review covers the literature published since the last review in 2021. Detailed reviews were carried out in 2002, 2008, 2014, 2017, and 2021. The report identifies and focusses on recent advances in all topics of dispersion and focusses on dispersant effectiveness, toxicity, and biodegradation. Published and peer-reviewed papers are included for this report. The report focusses on newly published developments.

Abstract

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 with high effectiveness. 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. These major issues are affected by aspects as described below.

There were 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 promoted and not hindered by the application of dispersants. Sometimes subsea dispersant effectiveness is added to the third pillar. In recent years, two new pillars have been added, that of the effects of dispersants and dispersed oil on human health and the effect of dispersants on marine snow and sedimentation. These factors have become important considerations.

Effectiveness remains a major issue with oil spill dispersants. Importantly, effectiveness varies with time as dispersed oil slowly rises to the surface. It is also 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. A new facet to this is the effectiveness of sub-sea dispersant injection. This will remain controversial for years. In the past years more and more articles indicate that the application during the BP DeepWater Horizon oil spill was **not** effective. This includes both sub-sea and surface applications of oil. Studies of the mass balances of the oil following the Deepwater Horizon spill show that the dispersant

effectiveness, either above or below the water surface is not necessary to account for the oil recovered, burned, sunken, or in other compartments of consideration.

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. Most toxicity studies of dispersed oil showed that chemically-dispersed oil was more toxic than physically-dispersed oil. Researchers found that the cause for this was the increased PAHs (polyaromatic hydrocarbons, a more toxic component of oil), typically about 10 to 100 times greater than from non-dispersed oil. Others noted the increased amount of total oil in the water column. No researchers found that the toxicity of chemically-dispersed oil was equal to or less than physically-dispersed oil.

The effect of dispersants on biodegradation is still a matter of dispute, however most studies showed dispersants inhibit biodegradation. Some industry-sponsored studies find the opposite. The reason dispersants may inhibit biodegradation 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.

***Note: A detailed report expanding on this summary is available. This larger report includes abstracts from key literature in the period from 2021 to 2023. Focus is placed on the larger issues of effectiveness, environmental toxicity, biodegradation, and human health effects.**

Executive Summary

What's New?

Increasingly it is becoming clear that dispersant injected during the Deepwater Horizon spill was not effective in either reducing the amount of oil that reached the surface nor in increasing biodegradation at depth. New publications on deep water spills show that there are almost no relevant studies covering the effect of high pressure. Most studies extrapolated surface study results on oil fate to deep water situations; this is incorrect.

The other main trends continue, and the 5 pillars of oil spill dispersants and their research continue on the same themes. These will be summarized below.

Effectiveness

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

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) 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. Alaska North Slope (ANS) crude oil is a 'medium' oil in terms of this category and is moderately 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 in controlled conditions. Currently, the only extensive work is being carried out in laboratories.

Considerable interest is still shown in sub-sea dispersant injection. No quantitative studies have shown that sub-sea dispersion is actually useful.

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. In recent times ASTM (American Society for Testing and Materials) 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 other than those conducted for PWSRCAC.

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:

- Salinity is an important factor in oil dispersibility; dispersibility decreases with decreasing salinity. Prince William Sound has low salinities in several areas, particularly areas affected by river inflows.
- Temperature is an important factor for dispersant effectiveness.
- As weathering increases for crude oils, dispersants become increasingly ineffective. Many laboratory testing results were conducted only on fresh oil. In reality, only weathered oil is ever treated at sea.

Analytical Techniques for Effectiveness

Analytical techniques as applied to dispersant effectiveness are a major issue. It should be noted that only ASTM or EPA (US Environmental Protection Agency) 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 many 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 spill 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.

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 2021-2023 (current period of this report) involved several studies. 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 all of the studies found that chemically-dispersed oil was more toxic than mechanically-dispersed oil.

The many toxicity studies of water-accommodated fractions (WAF) versus chemically-enhanced water-accommodated fractions (CEWAF) (oil plus dispersants) 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.

d) In most studies, it was found that CEWAF was from 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) The use of CEWAF protocols is being re-evaluated.

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 dispersion. This is especially true of the aquatically-toxic 2-ring and 3-ring PAHs.

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

k) Early life 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 PAH content may make it appear as though it is as toxic or more toxic than un-weathered oil. It is suggested here, that irrespective of the PAH calculations, weathered oil is usually 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) The results of a study using a single brand of dispersant should not be generalized to all dispersants. 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 on 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, such as in the deep-sea areas off Alaska. Studies now report that the use of dispersants lowers biodiversity generally.

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 an organism uptakes PAHs into biological tissues, the PAHs absorb energy from the light and then transfers this to dissolved oxygen radicals that cause cellular and tissue damage. This results in enhanced toxicity to many organisms. The tests of photo-enhanced toxicity show that oil and especially dispersed oil toxicity is increased by UV (ultraviolet) light. Increases of 1.5 to 4 are 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 at or near the water surface.

Testing Protocols

CROSERF (Chemical Response to Oil Spills: Ecological Research Forum) 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. Only PAH mineralization (that is complete degradation to CO_2) can be equated with toxicity reduction. Stimulation of alkane biodegradation, the easiest portion to biodegrade but also the least toxic, 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.

Past reviews found that most studies found that dispersants suppress biodegradation.

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.
- Encounters between oil droplets and bacteria is likely to be much more limiting at sea than in laboratory apparatus. This limits actual biodegradation.

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. Marine snow, without oil present, serves as an important food source for benthic organisms. Studies of past spills show that these spills precipitated increased amounts of marine snow with oil. 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. A new study shows that this number may be as high as 20%. In the recent review it was noted that marine snow also occurs as microaggregates of BOMAs or bacteria-oil microaggregates, which are harder to detect but contribute to bottom aggregation.

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 (Benzene, Toluene, Ethylbenzene, and Xylenes) 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. Further, mass balance studies show that there is little room left for dispersant effectiveness.

Dispersant proponents have often cited the Montara spill in Australia as an example of dispersant effectiveness. A recent court ruling on the Montara spill has shown that there was no or very little effectiveness of dispersants in this case and that the spilled oil impacted neighboring Indonesian islands.

NEBA (Net Environmental Benefit Analysis) has now changed its name to SIMA, Spill Impact Mitigation Assessment, which is the same as NEBA but purportedly adds some features. Most of these were already in various implementations of NEBA. Another variation on the theme is CRA (Comparative Risk Assessment) which looks mostly at risk.

Monitoring Dispersant Effectiveness

Improved 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. Some of these have been implemented.

Interaction with Sediment Particles

Several studies continued on oil-sediment interaction. Results are conclusive that dispersants increase the amounts of oil-sediment aggregates formed as a result of the increased number of 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. It should be noted that much of the Prince William Sound water has high sediment content. 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. A recent study on oil-sediment interactions suggests that as much as 20% of the oil from the Deepwater Horizon spill may have sedimented. It is important to note the difference between sedimentation by interaction with sediment particles and that of marine snow which is interaction with organic particles.

Dispersed Oil Stability and Resurfacing

Consideration of water-in-oil dispersion stability is an important matter. It is known that oil spill dispersions are 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. The results vary and to date there has been no definitive answer if the injection of dispersants during the Deepwater Horizon spill reduced droplet size or had any other effect. In fact, there is growing evidence that there was little effectiveness of the sub-sea injection.

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 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 from oil, 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.

- One study showed that there is some evidence that dispersion of the crude oil increased the emission rates of fine particulate matter that may carry toxic compounds.
- Another study showed that total number concentrations of airborne particles originating from the oil-dispersant mixture are 1 to 2 orders of magnitude higher than those of crude oil alone, across the entire nano-scale range, reaching 100 times for 20 nm particles (the smallest range).
- An epidemiological study showed that symptoms of dispersant exposure included coughing, the most prevalent symptom (19.4%), followed by shortness of breath (5.5%), and wheezing (3.6%). A recent study expressed concern for long-term respiratory conditions.
- One study concluded that the large quantity of dispersants used in the oil cleanup have been associated with human health concerns, including through obesogenicity, toxicity, and illnesses from aerosolization of the agents.
- A group of researchers studied the blood brain barrier (BBB) in mice, noting that oil spill-related compounds markedly affect BBB function, and that these changes may underlie the observed behavioral changes due to crude oil exposure.

Effect on Aquatic Organisms

The many toxicity studies of oil alone (WAF) and dispersants with oil (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. 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. Other times, the increase in PAHs does not correspond to the increase in toxicity.

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 works have suggested that CEWAF is more bioavailable than mechanically-dispersed oil. This is in addition to the note in h).
j) Species with translucent life stages that are susceptible to photo-enhanced toxicity are particularly vulnerable to increased water concentrations of PAHs caused by chemical dispersion.
k) Early life stages (embryonic and larval) of most species are much more susceptible to both CEWAF and WAF.
l) Weathered oil is generally shown to be less toxic to species (chemically- or mechanically-dispersed). In some infrequent circumstances, weathered oil has been shown to be more toxic to some species.
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) The results of a study using a single brand of dispersant should not be generalized to all dispersants. Many studies used Corexit 9500, however, other studies did not.

Biodegradation

The effect of dispersants on biodegradation is a very important topic as one of the stated objectives of using dispersants is to increase biodegradation. The effects of surfactants and oil dispersants on the rate and extent of biodegradation of crude oil and individual hydrocarbons have been extensively investigated, with mixed results. In some studies biodegradation is shown to be stimulated, in many there is inhibition and others observed no effects with the addition of dispersants. The effect of surfactants and dispersants depends on the chemical characteristics of the dispersants, the hydrocarbons, and the microbial community. Other factors such as nutrient concentrations (e.g., necessary nutrients for growth - such as certain nitrogen compounds), 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. It also noted that biodegradation of PAHs, the more persistent and toxic component of oil, have never been shown to be strongly 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.

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. This report concludes that only PAH mineralization can be equated with toxicity reduction.

A past review found that most studies conclude that dispersants suppress biodegradation (Fingas, 2017). This past 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.

Bacterial Population Shifts

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 (microbiota that degrade the alkanes, the simple oil compounds) 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.

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 of oil 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.

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 several 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 3D capability enables the calculation of dispersion. 3D models include consideration of the water column, whereas 2D models consider only the surface.

- 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.
- The models used on the Deepwater Horizon spill show contradictory results when it comes to effectiveness of deep-sea injection of dispersants.

New Dispersants

In this review, several 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. Few new application packages have been developed in recent years. Estimation of the aerial efficiency, namely how much falls on the slick versus the sea or how much blows away, has not been estimated.

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 absorption of PAHs.

Interaction with Microplastics

Researchers have found that dispersants increase oil interaction with microplastics and increase the movement of microplastics in the ocean.

Sinking

Researchers have proposed that the use of dispersants can increase the possibility of oil sinking.

Effects on Water Quality

Researchers have shown that dispersants in the water column disturbs water treatment systems, lowering the quality of the water output.

Fingerprinting

Researchers have shown that the addition of dispersants does not interfere with oil fingerprinting determinations.

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