

Briefing for PWSRCAC Board of Directors – September 2021

ACTION ITEM

Sponsor: Betsi Oliver, Danielle Verna, and the Scientific Advisory Committee

Project number and name or topic: 9550 Dispersant

1. **Description of agenda item:** Detailed reviews of dispersant research were carried out for the Council by Dr. Merv Fingas in 2002, 2008, 2014, and 2017. A 2021 summary review by Dr. Fingas briefly covers published literature since the last review in 2017. The report identifies recent advances in a wide variety of topics related to oil dispersion and focuses on dispersant effectiveness, toxicity, and biodegradation. Emphasis in this report is placed on aspects that relate to Alaska and Prince William Sound specifically. The report does not cover all aspects of dispersant knowledge but rather focuses on newly published developments.

This summary document will inform the Council's project to review and potentially update its position regarding the use of dispersants. The current position, adopted in 2006, states:

"After years of observing dispersant trials, dispersant effectiveness monitoring, advising and sponsoring independent research regarding chemical dispersant use, it is the position of the Prince William Sound Regional Citizens' Advisory Council that dispersants should not be used on Alaska North Slope crude oil spills in the waters of our region.

Until such time as chemical dispersant effectiveness is demonstrated in our region and shown to minimize adverse effects on the environment, the Council does not support dispersant use as an oil spill response option.

Mechanical recovery and containment of crude oil spilled at sea should remain the primary methodology employed in our region."

An appendix to this summary report gives notes on the published papers reviewed in its development and is available upon request. PWSRCAC maintains a comprehensive list of peer reviewed research related to dispersants on its website.

2. **Why is this item important to PWSRCAC:** Under the Oil Pollution Act of 1990 (OPA 90), PWSRCAC is authorized to participate in the development of plans and policy guidelines used in oil spill response. Chemical dispersant use has been a longstanding controversial topic. The use of dispersants may impact both the health of marine resources and human health. The use of dispersants also may compete with mechanical response for resources. PWSRCAC has invested significant time and resources in efforts to sponsor dispersant research, monitor dispersant research, and keep track of relevant regulations and policies governing dispersant use in the Prince William Sound region.

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The Council's current dispersant use position was enacted in 2006. Since then, much more scientific research on dispersants has been conducted and many lessons learned have resulted from using dispersants during major spills such as the 2010 BP Deepwater Horizon incident. This project to review and potentially update the Council's 2006 dispersant use position and supporting documentation is timely due to how much more is known about dispersants today.

3. **Previous actions taken by the Board on this item:**

<u>Meeting</u>	<u>Date</u>	<u>Action</u>
Note: Please request a list of actions prior to 2006 from staff.		
Board	5/2/06	Approved PWSRCAC Dispersant Use Statement.
XCOM	6/13/06	Approved the reported "Observers' Report: MMS Cold Water Dispersants Test conducted at the OHMSETT testing facility, February 28-March 3, 2006."
XCOM	12/11/06	Approved the report "Field Notes and Critical Observations from the OHMSETT Heavy Oil Dispersant Trials, October 13-16, 2003."
Board	1/22/09	Approved the dispersants literature surveys "A Review of Literature Related to Oil Spill Dispersants 1997-2008," "A Review of Literature Related to Oil Spill Dispersants Especially Related to Alaska 2002-2003," and the Solidifiers Literature Review titled "A Review of Literature Related to Oil Spill Solidifiers 1990-2009."
Board	9/16/10	Approved the issue paper on the use of dispersants in the BP Deepwater Horizon spill.
Board	9/15/11	Approve contracting with University of Southern Maine not to exceed \$70,000 for work on the toxicology of chemical dispersants in Alaska whales.
Board	9/15/11	Approve contracting with the Skidaway Institute of Oceanography at a cost of \$14,520 for work on the uptake and effects of dispersed oil droplets by zooplankton.
Board	5/3/12	Approved contracting with Spill Science for a comprehensive monitoring program for a cost of \$48,000.
Board	7/23/12	Approve contracting with NJIT for \$183,100 for dispersed oil biodegradation.
Board	5/2-3/13	Accept DFO final report on dispersed oil effects on salmon, cod, and herring.
Board	5/2-3/13	Accept final report on hydrocarbon uptake by spot shrimp from Dick Lee of the Skidaway Institute of Oceanography.
Board	1/23/14	Accept "Analysis of Oil Biodegradation Products" by Merv Fingas.
XCOM	4/16/15	Approve comments to EPA on Subpart J, Dispersants.
Board	5/17/16	Approved the report titled "Toxicology of Chemical Dispersants in Alaskan Whales."
Board	5/2016	Accept Dispersants SMART Monitoring Protocol document.
Board	3/7/17	Authorized a contract with Merv Fingas for the development of a comprehensive synthesis of dispersants research in an amount not to exceed \$65,000.
Board	5/3/18	Accepted the report titled "A Review of Literature Related to Oil Spill Dispersants, June 2017" by Merv Fingas of Spill Science, and the general version of the report titled "A Review of Literature Related to Oil Dispersants, September 2017" by Elise DeCola of Nuka Research & Planning Group, LLC.
XCOM	6/14/18	Approved report titled "A Review of Literature Related to Human Health and Oil Spill Dispersants."

4. **Summary of policy, issues, support or opposition:** In June 2020, a U.S. District Court Judge ruled that the Clean Water Act imposes on the EPA a mandatory duty to maintain an up-to-date oil spill response plan that reflects current science and technology. In August 2021, the court ruled that the EPA violated that duty since the relevant

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regulations have not been updated in more than 25 years. The EPA must now update and finalize its regulations, which includes the use of dispersants, by May 31, 2023. In July 2021, the EPA released a final rule on monitoring requirements for use of dispersants in Subpart J of the National Oil and Hazardous Substances Pollution Contingency Plan effective January 2022.

PWSRCAC provided extensive comments during the Alaska Regional Response Team planning effort to establish new policy for use of dispersants in state waters, which was adopted in January 2016, and presented to the Board by Linda Swiss in May 2016.

There appears to be strong support in updating the Board's position based on new information and science, and on the fairly high ranking this project received by the Board in the Long Range Planning process (rank 5 out of 17).

5. **Committee Recommendation:** The Scientific Advisory Committee recommends that the Board of Directors accept this report.

6. **Relationship to LRP and Budget:** Project 9550 Dispersants is in the approved FY2021 budget and annual workplan.

9550--Dispersants As of July 31, 2021

FY-2022 Budget

Original	\$32,000.00
Modifications	
Revised Budget	<u>\$32,000.00</u>

Actual and Commitments

Actual Year-to-Date	
Commitments (Professional Services)	
Actual + Commitments	<u></u>
Amount Remaining	<u>\$32,000.00</u>

7. **Action Requested of the Board of Directors:** Accept "A Summary of Dispersants Research: 2017-2021" by Dr. Merv Fingas, dated May 2021, as meeting the terms and conditions of contract number 955.21.01, and for distribution to the public.

8. **Alternatives:** None.

9. **Attachments:** Draft report titled "A Summary of Dispersants Research: 2017-2021" by Merv Fingas, dated May 2021.

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A Summary of Dispersants Research: 2017-2021

Prepared by Dr. Merv Fingas for PWSRCAC, May 2021

Foreword

This is an update report on dispersants and dispersant research. Detailed reviews were carried out for Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) in 2002, 2008, 2014, and 2017. This summary review briefly covers published literature since the last review in 2017. The report identifies recent advances in all topics of dispersion and focuses on dispersant effectiveness, toxicity, and biodegradation. Emphasis in this report is placed on aspects that relate to Alaska and Prince William Sound specifically. The report does not cover all aspects of dispersant knowledge but rather focuses on newly published developments.

An appendix to this summary report gives notes on the published papers reviewed in its development, and is available upon request. PWSRCAC maintains a comprehensive list of peer reviewed research related to dispersants on its website.

Abstract

The prime motivation for using dispersants is to reduce the impact of oil on shoreline. To accomplish this, the dispersant application must be successful and its 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 question that remains is the actual effectiveness during spills so that these values can be used in estimates and models in the future. These major topics are affected by issues as described below.

There were three 'issue pillars' for dispersants: effectiveness, toxicity, and biodegradation. Effectiveness, that percentage of oil that is put into the water by the use of dispersants, 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.

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. Sometimes subsea dispersant effectiveness is added to the effectiveness pillar.

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 are highly effective. A new facet to this is the effectiveness of subsea 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 spill was **not** effective. This includes both subsea and surface applications to oil. Studies of the mass balances of the oil following the BP Deepwater Horizon spill show most of the oil is accounted for using only those amounts burned, sunken, recovered, or lost through other known physical processes. Dispersant effectiveness does not account for any oil loss in some calculations. This fact raises the question of the true dispersant effectiveness.

The results of dispersant toxicity testing are similar to that found in previous years, namely that dispersants vary in their toxicity to various species. 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 (Polycyclic Aromatic Hydrocarbons, a more toxic component of oil), typically about 10 to 100 times, in the water column as a result of dispersant use. Others noted the increased amount of total oil in the water column. No researchers in this time period 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 that 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 with oil droplets which sinks to the bottom, 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

What's New?

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

The other main trends continue, and the five 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 this 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 cutoff' of effectiveness for dispersants exists. In fact, certain components of oil, such as resins, asphaltenes, and larger aromatics or waxes, are barely dispersible, if at all. Oils that are made up primarily of these components will disperse poorly when dispersants are applied. On the other hand, oils that contain mostly saturates, such as diesel fuel, will readily disperse both naturally and when dispersants are added. The additional amount of diesel dispersed when dispersants are used, compared to the amount that would disperse naturally, depends primarily on the amount of sea energy present. In general, less sea energy implies that a higher dose of dispersant is needed to yield the same degree of dispersion as when the sea energy is high. This should not be attributed to viscosity alone, but primarily to oil composition. Oils that typically contain larger amounts of resins, asphaltenes, and other heavier components are typically more viscous and less dispersible. 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 on controlled conditions. Currently, the only extensive work is being carried out in laboratories.

Considerable interest is still shown in subsea dispersant injection. No quantitative studies have shown that this 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, which 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; a test 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 the last time period, American Society for Testing and Materials (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, or destabilization 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 crude.

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.
- Paraffinic crudes are less dispersible.
- As weathering increases for crude oils, dispersants become increasingly ineffective.

Analytical Techniques for Effectiveness

Analytical techniques as applied to dispersant effectiveness are a major issue. It should be noted that only ASTM or U.S. Environmental Protection Agency (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 dioctyl sodium sulfosuccinate (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 solvents and proprietary surfactants called Tweens and Spans, however, the sensitivity is not as great. Studies in the case of the BP 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 subtidal life. Since that time, dispersants have been formulated with lesser aquatic toxicity. 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 2017-2021 (current period of this report) involved more than 27 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 BP Deepwater Horizon spill which attracted a large amount of interest and subsequent funding. 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) (oil mechanically dispersed into water) 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, patterns emerge in the results. Patterns may be specific to a study, or 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, the concentrations of CEWAF would initially be 10 to 100 times that of the WAF for an effective dispersion at sea.

- d) 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 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. Other times, the increase in PAHs does not correspond to the increase in toxicity.
- f) The use of CEWAF protocols is being re-evaluated by toxicologists.
- 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.
- j) Juvenile forms of most species are much more susceptible than adults of the same species to both CEWAF and WAF.
- k) Although weathered oil (chemically- or mechanically-dispersed) is generally shown to be less toxic to species, calculation of its PAH content may make it appear as toxic or more toxic than un-weathered oil. It is suggested here that, irrespective of the PAH calculations, weathered oil is almost always less aquatically toxic than its un-weathered counterparts.
- l) Some species are more susceptible to oil droplets than others, thus these species are more susceptible to chemically-dispersed oil than those species which are not susceptible to oil droplets.
- m) 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 on wildlife and other biota were carried out in this review's time period. Studies from 2017 to 2021 showed similar results to previous studies that corals are very sensitive to oil and particularly to dispersants and dispersed oil. The external membrane of coral is permeable to oil components and dispersants. Studies in the past two decades have repeated these findings. This should be cause

to reexamine 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.

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 of oil. Photo-enhanced toxicity consists of two mechanisms, the more important being 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 show that photo-enhanced toxicity of oil, and especially dispersed oil, is increased by UV light. Increases of 1.5 to 4 times were noted for physically-dispersed oil and from about 4 to 48 times for chemically-dispersed oil. Photo-enhanced toxicity is particularly applicable to organisms in the upper part of the water column.

Testing Protocols

Chemical Response to Oil Spills: Ecological Effects Research Forum (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 reevaluated with the current analytical and droplet size measurement capabilities. There is now some work ongoing.

Biodegradation

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. Biodegradation of PAHs, the most toxic component of oil, has never been shown to be strongly stimulated by dispersants.

Overall, many of the experimental systems used to investigate biodegradation might be considered inappropriate to represent the environment. 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 CO₂) can be equated with toxicity reduction. Stimulation of alkane biodegradation is not meaningful in the overall effects of oil spills. Alkanes are the easiest portion to biodegrade, but also the least toxic.

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 dispersants suppress biodegradation. 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

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 (those 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 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. The other result is that certain components of oil are degraded faster or slower than they would be if dispersants were not used.

Marine Snow Formation

Marine snow is a mucous-like agglomerate of organic material that can include oil. Marine snow, without oil present, serves as an important food source for benthic organisms. Marine snow production increases during spills and is further 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 the BP 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%.

Fate Impacted by Dispersant Use

The studies dealing with the oil fate as impacted by dispersants show that dispersants increase the amount of benzene, toluene, ethylbenzene, and xylenes (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. 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 spill has shown that there was no or very little effectiveness of dispersants in this case and that the oil impacted neighboring Indonesian islands.

Net Effects Benefit Analysis (NEBA) has now changed its name to Spill Impact Mitigation Assessment (SIMA), 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 Comparative Risk Assessment (CRA), 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 prescreen 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 oil-sediment aggregates formed; this happens because more droplets of oil are in the water column. 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 BP 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 sometimes temporary and resurfaced slicks can appear. Further, the amount of oil entering the water has been shown to be highly variable, which has 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. There is one paper during this review period which addresses this and models the entire process of spill dispersion.

Subsurface 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 BP Deepwater Horizon spill reduced droplet size or had any other effect. In fact, there is growing evidence that there was little effectiveness of the subsea 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 to children from touching beach sand that had been contaminated by oil and/or dispersant was low.
- The health risk from approved seafood was low and maybe less than the risk from inland seafood.
- 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.
- DOSS, an ingredient of Corexit, was found to be an obesogen; however, one would need to ingest DOSS to cause this effect.
- One study showed 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 one to two 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 as the most prevalent symptom (19.4%), followed by shortness of breath (5.5%), and wheezing (3.6%).
- 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.

Modeling

Modeling is increasing and becoming a source of information beyond its 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 three-dimensional (3-D) oil spill models are published, whereas before, most were two-dimensional (2-D). This 3-D capability enables the calculation of dispersion. 3-D models include consideration of the water column, whereas 2-D 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 was 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 BP Deepwater Horizon spill, especially that of the subsea 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.
- Overreliance on models to understand natural systems can occur in the absence of actual data.
- The models used on the BP 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 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.

Fate of Dispersants

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

- 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.

NAS Dispersant Review

The U.S. National Academy of Sciences conducted a review of dispersants in the past year (NAS 2019). This was a limited review because the literature body is extensive (greater than 2,500 papers) and it would be difficult to review it all. Instead, the Academy members reviewed issues and addressed questions posed to the committee based on the experts' knowledge and using some of the published reviews.

There are several shortcomings of the report. It should be noted that this was not an independent study but was funded by a number of government agencies and the American Petroleum Institute. Members of the panel were chosen with assistance from the sponsors, they were not chosen independently.

Secondly, the exercise was not a detailed review of the literature, rather it was addressing a number of issues set by the sponsors. A detailed look at some of the prime issues identified by PWSRCAC reviews in the past (Fingas 2014, 2017) shows that only some of this literature was used. Specific examples of this will be detailed below.

The issues surrounding dispersants remain the same: effectiveness, toxicity, and long-term benefits. In recent years, the biodegradation of oil and the health effects on humans have been added as serious concerns. Specific comments and comparisons on each of these facets appear below:

1. Effectiveness - Effectiveness is largely unaddressed in the NAS 2019 report. It did not form part of the task. This is not optimal, as effectiveness is a major issue and a cornerstone issue in the use of dispersants. Lack of effectiveness in many cases makes the application considerations inappropriate.
2. Aquatic Toxicity - Much of the literature noted in the reviews by Fingas in 2014 and 2017 was not mentioned, analyzed, or noted. This is important as the data in reports such as Fingas 2017 were extensive and found that dispersant addition to oil caused further toxicity, above the oil itself. Further there is great emphasis on the Toxic Units Model, a minority model which is known to be not representative of hydrocarbon toxicity. It always predicts that weathered oil is much less toxic than fresh oil.
3. Human Health - Human health is reviewed briefly and only the Gulf of

Mexico workers studies are mentioned in detail of the many new studies noted in the Fingas 2017 review. Most of the other (about 20) references are not dealt with.

4. Literature Review - Very little of the current literature was reviewed; most references were made to dispersant-positive studies. The Fingas 2017 review noted dozens of data tables and corresponding discrepancies. These discrepancies in the literature were barely mentioned, or written off as bad research.
5. In-depth Analysis - There was no in-depth analysis of any topic. The report simply looked at an issue (or question) and made summary statements about it. Only in the case of biodegradation was any literature cited, and then it was an incomplete summary. An example of data found in the Fingas 2017 report is shown in Table 1. It should be noted that this is part 1 of 6 of the table and the full table can be found in the 2017 report. None of these aquatic data points were specifically noted in the NAS 2019 report nor were any of about 20 researchers cited in the Fingas 2017 report cited in the NAS report.
6. The large number of references listed are not actually used, just noted.
7. One telling quote: "the effect of SSDI [Subsea dispersants injection] on biodegradation of liquid oil in the subsurface intrusion layers is minor inasmuch as only a small fraction of liquid oil was trapped in the layers with and without SSDI." This basically says that SSDI did not work! The summary statements later on do not mention this fact.

Research Needs (based on this summary report)

1. Continuing research on human and environmental toxicity
2. Re-examine effectiveness tests, continue effectiveness testing using standard protocols
3. Re-examine old research before proceeding with new research
4. Examine in more detail the applicability of dispersants to Alaska and Prince William Sound in particular
5. Focus on using real data rather than modelled data and small-scale tests

Table 1 Biodegradation Studies							
Author(s)	Year	Oil Type	Time	Dispersant	Notes	Funder	Effect
Bacosa et al.	2015a	Louisiana	36 d	Corexit 9500		Gov't & Res.	neut.
Bacosa et al.	2015b	Louisiana	36 d	Corexit 9500	Corexit inhibited some bacteria	Gov't & Res.	neg
Bagby et al.	2015	Macondo		none		Gov't	
Bookstaver et al.	2015	Octane	72 h	Corexit 9500	Corexit inhibited the bacteria	Gov't & Res.	neg.
Brakstad et al.	2015	Macondo	64 d	Corexit 9500	smaller droplets degraded more	Industry	pos.
Cappello et al.	2014	Arabian	2 d	Biosurfactant	Biosurfactant increased microbes	Gov't & Res.	
Crisafi et al.	2016	Arabian	14 d	not specified	Washing agent decreased microbes	Gov't & Res.	neg.
Cuny et al.	2015	Russian	286 d	Finasol	Dispersant did not increase biodegradation	Gov't & Res.	neg.
Kleindienst et al.	2016c	Macondo	6 wk	Corexit 9500	over 31 wks, dispersant suppressed biodegradation	Gov't & Res.	neg.
Olson et al.	2017	Macondo	28 d	Corexit 9500	natural seawater degraded, little diff with disp.	Gov't & Res.	neut.
Ortmann and Lu	2015	Macondo	5 d	Corexit 9500	Dispersant and oil changed microbial composition	Gov't & Res.	neg.
Overhold et al.	2016	Marlin	14 d	Corexit 9500	Growth and biodegradation inhibited t by 34% and 40%	Gov't & Res.	neg.
Overhold et al.	2016	Marlin	14 d	Corexit 9500	Growth increased by 10%	Gov't & Res.	neg.
Pietroski et al.	2015	Macondo	5 d	Corexit 9500	initial reduced mineralization by 12%	Gov't & Res.	neg.
Pietroski et al.	2015	Macondo	5 d	Corexit 9500	after 2 weeks reduced mineralization by 88%	Gov't & Res.	neg.
Prince et al.	2015	Alaskan NS	62 d	Corexit 9500	increased biodegradation over slick	Industry	pos.
Prince et al.	2015	Alaskan NS	62 d	Finasol	increased biodegradation over slick	Industry	pos.
Prince et al.	2015	Alaskan NS	62 d	Slickgone	increased biodegradation over slick	Industry	pos.
Rahsepar et al.	2016	Macondo	30-50 d	Corexit 9500	decreased biodegradation/ increased aromatics	Gov't & Res.	neg.
Rahsepar et al.	2016	Macondo	30-50 d	Corexit 9500	decreased biodegradation/ increased aromatics	Gov't & Res.	neg.
Seidel et al.	2016	Marlin	6 wk	Corexit 9500	Decreased biodegradation/ Little DOSS deg	Gov't & Res.	neg.
Størdal et al.	2015a	Troll	48 h	Natural disp.	feces slowed biodegradation	Gov't & Res.	
Størdal et al.	2015a	Troll	48 h	Natural disp.	oiled feces increased biodegradation	Gov't & Res.	
Størdal et al.	2015b	Troll	48 h	Natural disp.	feces slowed biodegradation	Gov't & Res.	
Størdal et al.	2015b	Troll	48 h	Natural disp.	oiled feces increased biodegradation	Gov't & Res.	

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