[redacted]

To RPP/OACETT:

As outlined under the Technology Report Guidelines, I am submitting the attached report entitled *The Use of Oil Dispersants in Petroleum Cleanup Efforts*. This will demonstrate a level of engineering technology equal to that required of an Engineering Technologist and my overall technical problem-solving abilities.

This report examines the environmental effects and associated concerns with utilizing oil dispersants in response to an oil spill in marine environments. While the dispersant may appear effective to the naked eye, in some cases, it can make the water more toxic than it was originally with the untreated oil alone due to harmful break-down products. Discussed are the application processes, chemicals used, ecological factors, short-term effects, and the potential long-term effects.

I really enjoyed conducting this research and I hope you have as much fun reading this report as I did in writing it.

Sincerely yours,

[redacted]

[redacted]

Enclosure: Technology Report

TECHNOLOGY REPORT

ON

THE USE OF OIL DISPERSANTS IN PETROLEUM CLEANUP EFFORTS

[redacted]

OACETT Membership No.: [redacted]

[redacted]

The report examines the use of oil dispersants in petroleum cleanup efforts. Topics that are discussed include: application processes, effectiveness under different temperatures, reactivity with oil and water, toxicity and reformulated chemicals, potential health problems, and the overall short-term and long-term effects. An overall review of the practicality of their use concludes the report.

Declaration of Authorship

I, [redacted], confirm that this work submitted for assessment is my own and is expressed in my own words. Any uses made within it of the works of any other author, in any form (ideas, equations, figures, texts, tables, programs), are properly acknowledged at the point of use. A list of the references used is included.

[redacted]

[redacted]

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DISPERSANT USE IN OIL SPILL CLEANUP EFFORTS IN MARINE ENVIRONMENTS

TECHNOLOGY REPORT PROPOSAL

FROM:

[redacted]

DISCIPLINE:

RESOURCES

DATE:

[redacted]

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With oil spills occurring everyday and some of the largest in history occurring in recent years, cleanup practices have become a very important part of the petroleum industry. With this said, the use of oil dispersants in cleanup processes in marine environments has been subject to much debate. In order to effectively decide whether, or not, the use of dispersants should be an acceptable practice in petroleum cleanup efforts, and under what circumstances they should be utilized, it is essential that each aspect of the processes involved is analyzed carefully and with respect to case-by-case studies due to its variety in nature.

The purpose of this report will be to demonstrate that modern oil dispersants, in particular Corexit® 9500, 9527 and 9580, despite appearing efficient in the immediate cleanup of water sources, can have significant impacts on the environment and careful consideration should be given to the following: chemical structure, application processes, ecology, short-term effects, and the overall long-term effects. Legalities and limitations around dispersant use will also be discussed.

Oil dispersants, which are a complex mixture of chemicals used to break up oil into stable droplets, are commonly used in response to an oil spill. Through the analysis of extensive research and data on the use of dispersants, including areas of focus such as: toxicity and reformulated chemicals, treatment processes, effectiveness under different temperatures, reactivity with oil and water, potential health problems, effects on marine life and habitat, and the impacts on water sources subject to extended contamination, the overall effectiveness of oil dispersants can be assessed.

Carefully analyzing real-world cases like the Torrey Canyon spill, the Deepwater Horizon spill, and the Exxon Valdez accident, which involved the controversial use of

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Corexit® dispersants, it becomes evident that oil dispersants, while appearing effective under certain conditions, can have serious environmental impacts. Data collected in several toxicity studies including controlled laboratory screening, as reported by a variety of health and research institutes, including: the National Oceanic and Atmospheric Administration (NOAA), the United States EPA, and the National Institute for Occupational Safety and Health (NIOSH), will show that oil dispersant effectiveness is influenced my many factors, not limited to chemical composition, physical properties, application processes, and modeling accuracy.

Due to the known toxic effects of several of the chemicals found in oil dispersants, such as Corexit® 9500, 9527 and 9580, which are currently authorized under the Canada Oil and Gas Operations Act, dispersants should only be used when mechanical means, such as skimmers and oil-water separators, are not sufficient. If chemical dispersants are being considered in oil spill cleanup efforts at sea, careful consideration must be given to several factors, such as: weathering, oil type, dispersant potential, wave activity, application processes, birds and marine life, and a variety of other environmental conditions. In addition to this, government agencies must have more stringent guidelines on using chemical dispersants in marine environments. When comparing to mechanical cleanup devices, chemical dispersants should be viewed as a last resort and subject to stringent regulation as their negative impact on marine environments and the health of a variety of species is well documented.

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---------- Forwarded message ---------

[redacted]

OACETT

Dear [redacted]

Your Technology Report Proposal has been ACCEPTED as SATISFACTORY and you have been assigned a one year deadline to submit the Technology Report - [redacted]

The Technology Report can be submitted through your OACETT portal account by selecting your C.E.T. application.

Please consult the Technology Report Guidelines found here for more information.

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ABSTRACT

With oil spills occurring every day and some of the largest in history occurring in recent years, cleanup practices have become a very important part of the petroleum industry. With this said, the use of oil dispersants in cleanup processes at sea has been subject to much debate. To effectively decide whether, or not, the use of dispersants should be an acceptable practice in petroleum cleanup efforts, it is essential that each aspect of the processes involved are analyzed carefully and with respect to case-by-case studies due to its variety in nature. The purpose of this report is to assess the effects of modern oil dispersants, such as Corexit® 9500 and 9527, in their use to cleanup water sources, and the potential impacts they can have on the surrounding environment. Careful consideration should be given to the following: chemical structure, application processes, ecology, short-term effects, and the overall long-term effects. The importance of always considering these factors before implementing chemical dispersants is outlined in the report. Because oil spills are typically unexpected, it is important for petrochemical companies to have an emergency response strategy that reflects a comprehensive understanding of what cleanup methods are most effective and whether, or not, oil dispersants are practical under certain conditions.

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TERMINOLOGY AND ACRONYMS

ADDS - airborne dispersant delivery system

ACP - Area Contingency Plan

BP - Beyond Petroleum, formerly known as British Petroleum

Corexit® 9580, Corexit® 9500, and Corexit® 9527 - chemical dispersant/cleanup products manufactured by NALCO®, for the purpose of oil cleanup efforts; these product lines are also recognized as EC9580A, EC9500A, and EC9527A.

cSt - centistokes

DWH - Deep Water Horizon

EPA - Environmental Protection Agency; the EPA is based in the United States of America

EVOS - Exxon Valdez Oil Spill

Hydrophobic - repels or does not readily show an affinity to water; does not readily mix with water

Hydrophilic - expresses an affinity to water; readily mixes with water molecules

ITOPF - International Tanker Owners Pollution Federation Ltd.

LC50 - refers to the dose of a specific chemical product or mixture that will cause mortality to 50% of a given group of test species

LOAEL - the lowest observed adverse effect level

MSDS - Material Safety Data Sheet

NALCO - National Aluminum Company

NCP - National Oil and Hazardous Substances Pollution Contingency Plan; also referred to as the National Contingency Plan

NOAA - National Oceanic and Atmospheric Administration

NIOSH - National Institute for Occupational Safety and Health

OSC - Oil Spill Commission

Olfactory - the sense of smell or process or smelling

ppt - parts-per-thousand

ppm - parts-per-million

Payload - carrying capacity of an aircraft or vessel/space ship

Pour point - lowest temperature at which a liquid becomes semi-solid

RRT - Regional Response

Team **RCP** - Regional

Contingency Plan **Surfactant** -

surface-active agents

UVF - ultra-violet fluorometry

WHOI - Woods Hole Oceanographic Institution

THE USE OF OIL DISPERSANTS IN CLEANUP EFFORTS

INTRODUCTION

One of the most controversial issues in relation to the environmental impacts of the petroleum industry is the occurrence of oil spills and, more specifically, what to do when one takes place. Oil dispersants, which are a complex mixture of chemicals used to break up oil into stable droplets, are commonly used in response to an oil spill. The use of dispersants in oil spill cleanup efforts has been subject to much debate as many feel that, while they are effective in dispersing oil spilled on the surface of the water, they are believed to make the water more toxic than it was with the untreated oil.

There has been extensive research on the use of dispersants, including areas of focus such as: toxicity and reformulated chemicals, treatment processes, effectiveness under different temperatures, reactivity with oil and water, potential health problems, effects on marine life and habitat, and the impacts on water sources subject to extended contamination. Through studying this subject matter and carefully analyzing real-world cases like the Torrey Canyon spill, the Deepwater Horizon spill, and the Exxon Valdez accident, which involved the controversial use of Corexit® dispersants, it becomes evident that oil dispersants, while appearing effective under certain conditions, can have serious environmental impacts.

Oil spills occur every day and have become an important part of the petroleum industry's operation. For these reasons, it is essential that oil companies have a better understanding of the risks involved with dispersant use, so that cleanup efforts are more effective when future spills occur.

METHODOLODY

I. CHEMICAL COMPOSITION AND PROPERTIES

When analyzing the use of oil dispersants at sea, it is important to have a basic understanding of the chemical behaviour of oil and water and how these substances react differently with one another under varying conditions (i.e. surface area, oil composition, turbulence, and type of chemical dispersant). It is from the general understanding of the chemical behavior of oil and water that dispersants can be developed and implemented into oil spill cleanup efforts. With this said, the development of modern dispersants has not come easily, and it is through first-hand experience with cases like the Torrey Canyon spill and the Exxon Valdez oil spill (EVOS) that a dispersant like Corexit® has been reformulated and refined to produce less destructive results.

Behaviour and Properties of Oil

In the case of an oil spill at sea, the oil can spread very quickly, forming a slick, with varying thickness depending on the type of oil and the available area for spreading. With high water activity due to wind and other turbulent influences, the slick can be broken up into spherical droplets, which range in size from just a few micrometers to several millimeters (*Using Oil Spill Dispersants on the Sea*, 1989). The oil droplets can be stabilized by natural surface-active agents, referred to as surfactants, present in the oil, or contributed by the sea-surface micro-layer in the region where the oil is spilled. The large increase in the oil–water interface, due to oil droplet formation, increases the biodegradation of the oil through natural occurring micro-organisms (Brandvik & Daling, 1998). The surfactants stabilize the droplets as the hydrophobic (little or no affinity for water) region of the surfactant molecule is situated in the oil phase and the hydrophilic (affinity for water) region is oriented in the water phase, which in turn diminishes the interfacial tension.

Chemical Composition and Properties of Dispersants

Fundamentally, an oil dispersant will be comprised of one or more surfactants, which will contain molecules that are made up of both hydrophilic and hydrophobic regions, and a solvent to reduce viscosity and guide dispersal (*Using Oil Spill Dispersants on the Sea*, 1989).

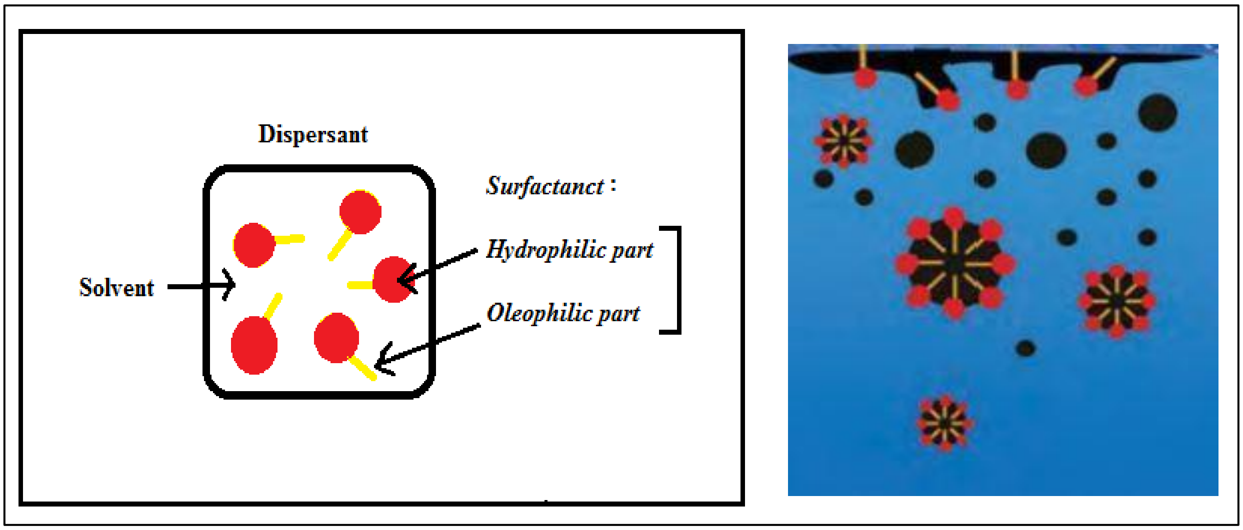

Figure 1. Orientation of dispersant molecule (*ITOPF*, 2011). The right image shows how the surfactant molecules migrate into the oil/water interface and reduce surface tension, allowing small oil droplets to break away from slick.

Oil dispersants can be used to enhance the rate of natural dispersion. Dispersants remove the oil slick from the sea surface and dilute the oil to small, less reactive, droplets in the water column. Essentially, the chemical dispersants increase the amount of surfactant available and can reduce oil-water interfacial tension to significantly low values; therefore, requiring only a small amount of mixing energy to increase the surface area and break the slick into droplets (*Using Oil Spill Dispersants on the Sea*, 1989). In addition to this, chemical dispersants are able to limit and prevent the coalescence of oil droplets in the water. The interface, which is stabilized by the surfactant, allows the droplets to remain stable, despite colliding frequently with adjacent droplets. As outlined in "Chemistry and Physics of Dispersants and Dispersed Oil" (1989), these stabilizing factors are able to reduce the affinity of hydrophilic solid particles (i.e. sediments). Currently, there are only 22 authorized chemical dispersants recognized under the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), as outlined by the EPA (*NCP Product Schedule*, 2013).

Early Dispersant Use

The earliest chemical dispersants used in oil spills on sea were aromatic hydrocarbon-based products, which were initially designed for the purpose of cleaning tanker holds and bilges (*Ecotoxicology and Environmental Safety*¸ 1995). These dispersants were used in the case of the Torrey Canyon spill, in which the supertanker *SS Torrey Canyon* ran aground on the southwest coast of the United Kingdom in 1967, leaking over 30 million gallons of crude oil into sea (*ITOPF*, 2011). Research showed that these earlier dispersants were more toxic to marine life than the oil was. The first generation of dispersant products, which were introduced throughout the 1960's were chemically similar to industrial cleaners and degreasers with notably high aquatic toxicity (*ITOPF*, 2011). For this reason, they were prohibited from use in oil spill response and further developments in dispersant mixtures focused on incorporating fewer toxic surfactants that were non-ionic (dissolving in non-polar solvents) and contained solvents such as glycol ethers, which are common in cleaning compounds (*Ecotoxicology and Environmental Safety*¸ 1995).

II. APPLICATION PROCESSES

There are a variety of application methods that can be used in deploying dispersants on oil spilt in open water. Each application method offers different advantages and disadvantages, which must be taken into consideration in oil spill response efforts. The precise circumstances under which each application process is most useful should be known if adequate emergency preparedness is required.

Vessel Spraying

Vessel Spraying refers to spraying the dispersants on the surface of the water from a watercraft or on-sea vessel. The dispersants are typically sprayed through a set of nozzles mounted on spray arms, which are attached to the boat, as shown in **Figure 2**. In terms of the mechanical

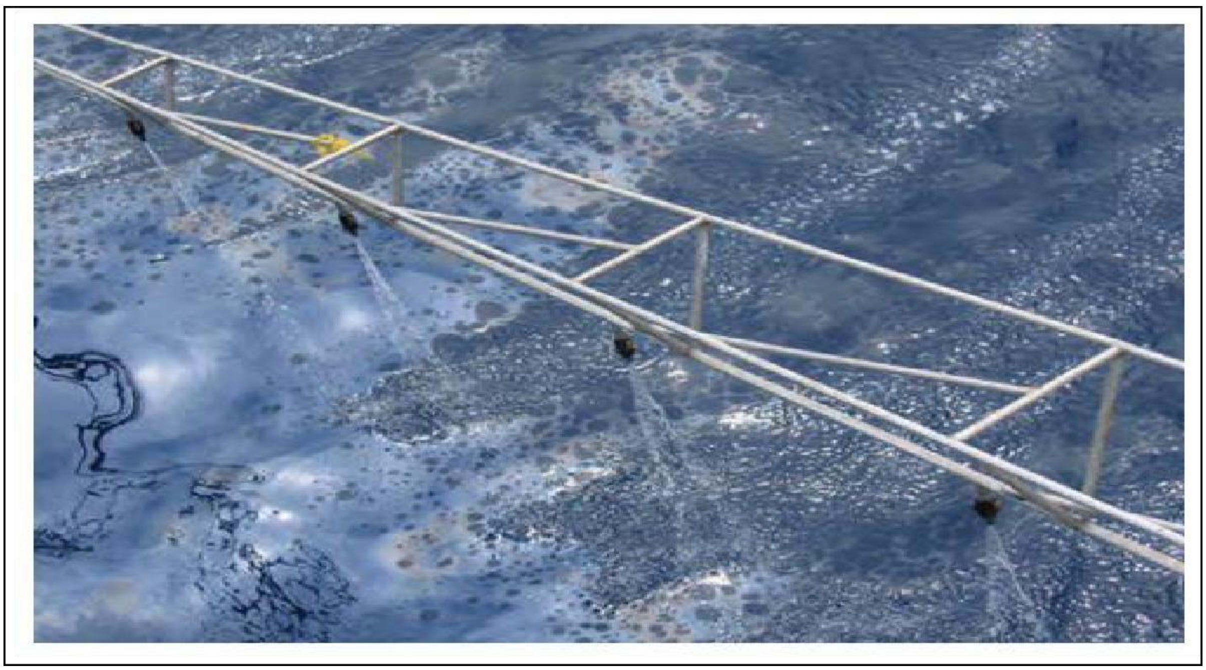

Figure 2. Application of dispersant from vessel mounted spray arms (*ITOPF*, 2011). configuration, pumps deliver dispersant from a storage tank to the spray arm, which is fitted with a set of evenly distributed nozzles, aimed at producing a uniform

spray pattern (*Use of Dispersants to Treat Oil Spills*¸ 2011). These types of spray units can be permanently mounted on the vessel or can be installed temporarily, if a portable system is used.

In order to increase efficiency, spray arms are generally mounted towards the front of the vessel, avoiding the bow wave pushing the oil beyond the width of the spray pattern (*ITOPF*, 2011). In addition to this, mounting the spray arms on the bow enables the boat to travel at greater speeds and, as the freeboard (distance from waterline to the upper deck level) is often greater at the bow, the spray arms can become longer. This mounting method creates an optimal encounter rate, which refers to the amount of oil that can be treated, while limiting the dispersant payload.

It is important to note that fire hoses are sometimes used to apply concentrate dispersants diluted in the water stream; however, because of high flow rates, it can be difficult to apply the dispersant in uniform rates, limiting optimum dilution (*Use of Dispersants to Treat Oil Spills*, 2011). It is critical that spray systems deliver relatively uniform dispersant droplets that are of the correct size. It is essential to efficient dispersion that the droplets are large enough to overcome the natural effects of wind drift and evaporative loss, while not being so large that they are unable to orientate themselves in the oil/water interface. Studies have shown that, in most cases, an optimum droplet size is between 600µm and 800µm; however, this can vary with oil type and water conditions (*Use of Dispersants to Treat Oil Spills*, 2011). According to the NOAA, dispersants that are applied using spraying systems (both vessel and aerial) should be operated at a target treatment rate of 5 gal per acre of oil, to achieve a dispersant to oil ratio of 1:20; once again, application rates will vary with spill size and oil conditions (*Review/Select Potential Options and Products*, 2003).

The main advantages of vessel spraying, over other application methods, are: availability, ease of loading, fairly accurate application to specific areas of a slick, and cheaper cost, in comparison to a method like aerial spraying (ITOPF, 2011). On the other hand, significant limitations of vessel spraying include: difficulty with larger spills, due to low treatment rates, and weaknesses in locating the heaviest concentrations of oil from the bridge (command room) of a vessel.

Aerial Spraying

The deployment of dispersants from an aircraft is referred to as aerial spraying. Broadly speaking, there are 3 types of fixed-wing aircrafts that can be used in dispersant applications: modified agricultural or pest-controlled operations aircrafts, adapted cargo aircrafts, and helicopters with fixed spray systems. Aerial spraying systems can include: spray buckets, which have a payload of 7 to 21 liquid barrels (deployed from helicopters), specially equipped DC-3 aircraft, with a payload of 30 liquid barrels, and a cargo aircraft, which can be fitted with an airborne dispersant delivery system (ADDS) pack, with a payload of up 150 liquid barrels (*Review/Select Potential Options and Products*, 2003). In choosing the ideal aircraft, selection will be based on the size and location of the spill. Aircrafts will require safe operation at low altitudes (15 to 30 meters) and slow speeds (25 to 75 m/s), while being highly maneuverable (*Use of Dispersants to Treat Oil Spills*, 2011). Consideration must also be given to fuel consumption, payload capabilities, and the distance between the spill and the operating base, when choosing a suitable aircraft. As stated earlier, spraying should be operated at a target treatment rate of 5 gal per acre of oil, to achieve a dispersant to oil ratio of 1:20 (*Review/Select Potential Options and Products*, 2003). Discharge units, mounted on aircrafts, usually contain either pressure nozzles or wind driven rotator units, uniformly spaced, producing dispersant droplets of the optimum size. These spraying units, and aerial spraying in general, offer significant advantages, such as: rapid response, high treatment rates, and optimum dispersion. However, the high costs associated with aerial methods, due to specialized operations and fuel consumption, can become an issue.

Figure 3. DC-3 aircraft applying dispersant to oil spilled in the Gulf of Mexico during the DWH spill (*National Geographic*, 2010).

Underwater Application

In the case of the DWH spill, the initial dispersant method used was surface spraying; however, as over 200,000 gallons of dispersant were applied in the first two weeks, posing a potentially huge exposure of toxic chemicals to marine life, scientists began to look at alternatives (*Oil Spill Commission*, 2012). The most favourable of these was the unprecedented method of underwater dispersant application. As oil was being ejected from a deep wellhead, due to the blowout that occurred, the reactions (both physically and chemically) that were occurring in the water were different than that seen in cases where oil was spilled on the surface. When oil and gas mixtures are released from wellhead, deep within the sea, liquid oil droplets of varying sizes can form and rise toward the ocean surface. Deep below the water's surface, the smaller droplets can become as dense as the surrounding water and are pushed away in a lateral direction due to prevailing ocean currents (*WHOI*, 2011). With this said, most of the droplets are too large to be pushed away and will not biodegrade overtime. Scientists, working under the response efforts of BP, theorized that if dispersants were applied underwater and worked ideally, the vast majority of the liquid oil would be broken up into neutrally buoyant droplets by the surfactants and carried away before reaching the surface. In addition to this, if the dispersant worked perfectly, the droplets would become small enough to be biodegraded by bacteria.

Unfortunately, post-application monitoring discovered that, despite the dispersant mixing with a significant volume of the small droplets in the deep-water hydrocarbon plume, which was at a depth of 1100 meters, several months after application, the oil/dispersant mixture had not yet biodegraded (*WHOI*, 2011). Scientists concluded that they were unable to distinguish between the oil droplets that were coated in surfactant and the surfactant that was floating freely on its own; therefore, could not state whether the dispersant worked as planned or did not attach to the oil as indented.

Figure 4, below, demonstrates (at a high level) how the dispersants were expected to work (theoretically) and what the actual results were shown to be.

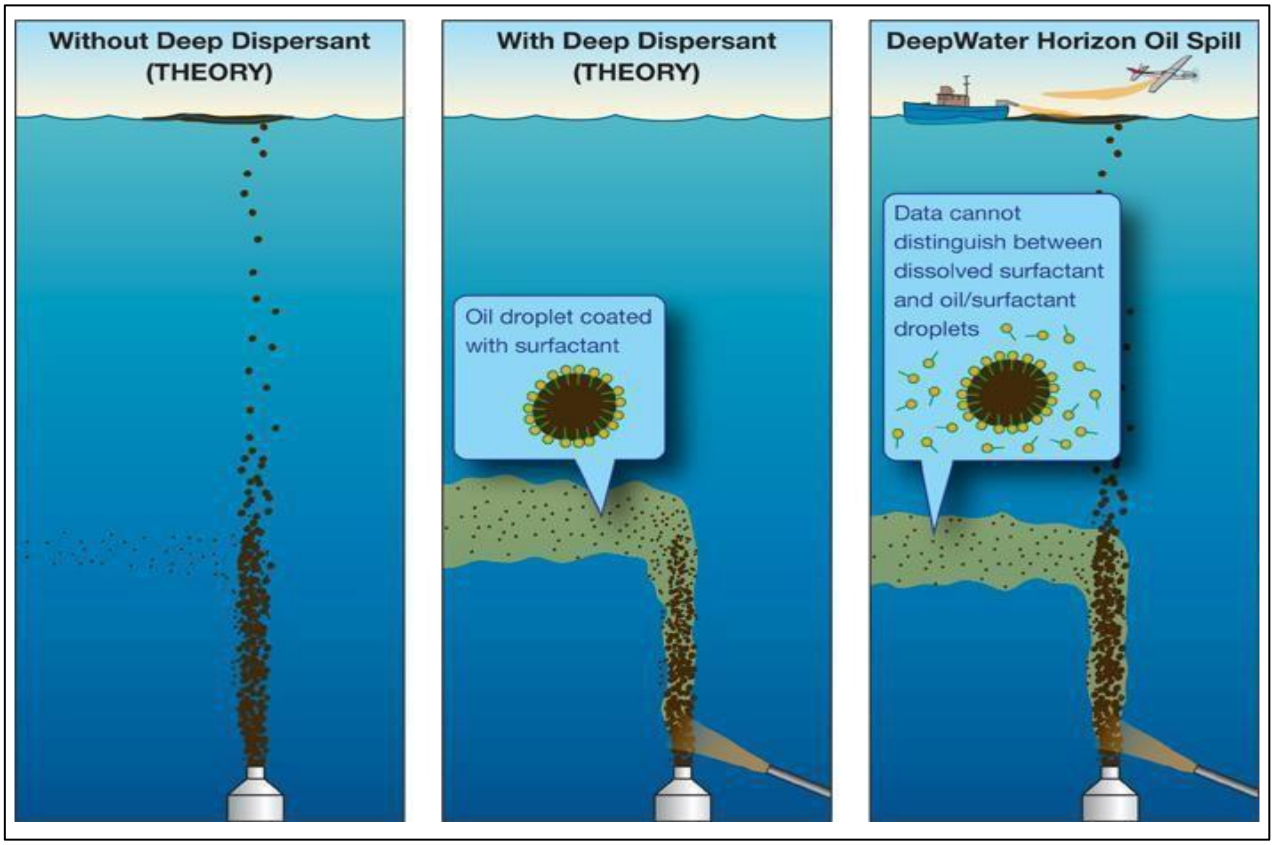

Figure 4. Deep dispersion application in DWH spill (*WHOI*, 2011); theoretical use (center) and observed results (right).

Figure 5 on the following page shows how the dispersant was applied under the surface of the water using coiled tubing, which was sent down from a construction vessel, delivering oil dispersant to the source of the leak; activity was observed using underwater remote- operated vehicles.

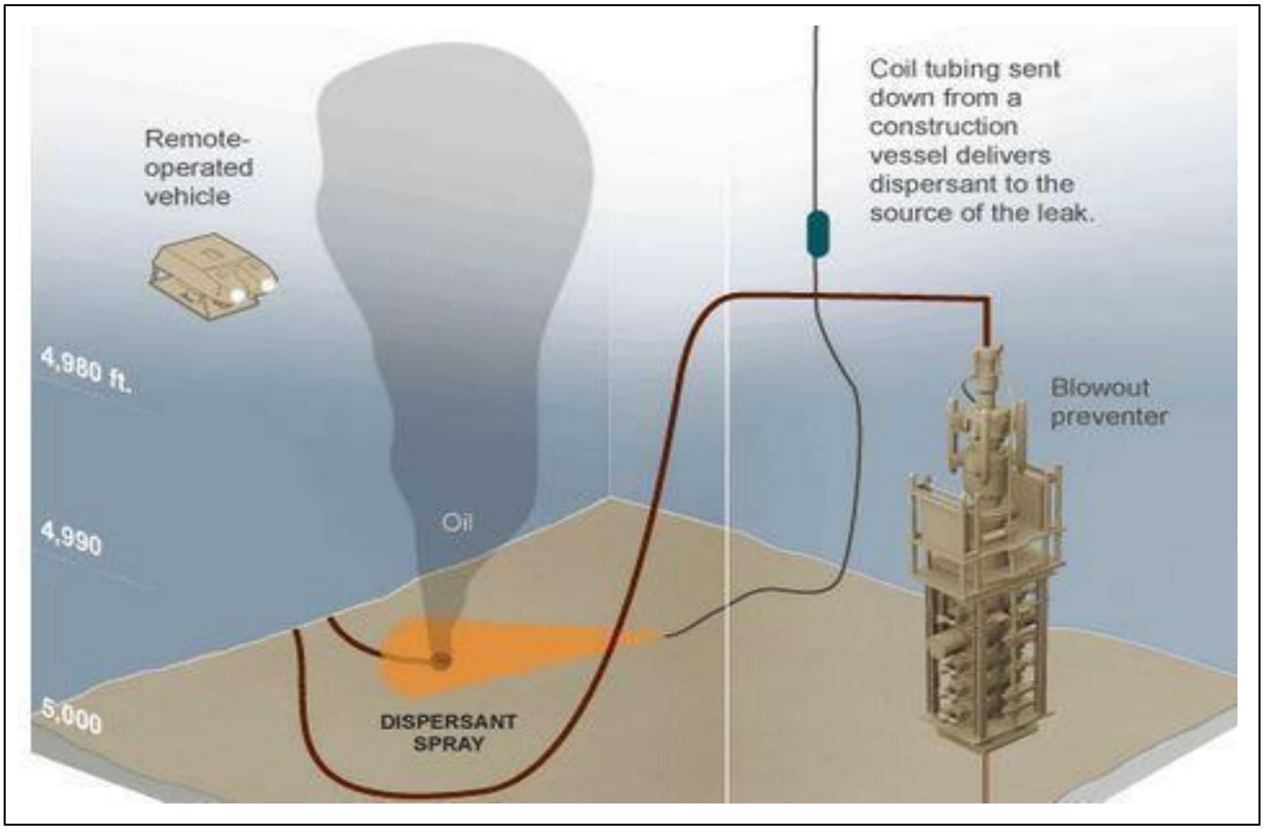

Figure 5. Delivering dispersant to DWH leak source (*OSC*, 2012).

Logistics and Operation

To ensure that all logistics are in place, it is essential that the trained operators, who are applying the dispersant, are thoroughly prepared. First off, in spraying applications (both aerial and vessel) a spotter aircraft should be utilized, identifying any heavily concentrated areas of the spill, posing the greatest threat level (*ITOPF*, 2011). In using a spotter aircraft, communication is key as cleanup teams want to limit overspray of dispersant, while being as effective and efficient as possible (i.e. accuracy). It is also important that there are relief crews available as flying at such low altitude, maneuvering just above the surface of the water, can be very physically and mentally demanding.

For those working on vessels, organization is very important. Operators want to maximize the amount of spraying that can be done during daylight hours, while keeping on track with routine maintenance on aircrafts and spraying equipment. It is likely that vessels will need to be re- supplied with dispersant and fuel, while provisions should be made to other equipment such as pumps and tankers, which are necessary in dispersant cleanup processes. Careful attention must be given to proper storage of dispersants as well. A temperature of -15º C and 30º C is considered optimum for storage of most dispersants; those that have been diluted with sea water should not be re-stored (*ITOPF*, 2011).

Being organized and prepared is crucial to having control over dispersant applications. Following proper safety parameters and recommended application, maintenance, and storage methods, cleanup teams are likely to see more effective results, while limiting the controversy around dispersant use.

III. MONITORING AND PREDICTIVE ANALYSIS

In dispersant application, one of the most important steps is to regularly monitor the effectiveness of chemical dispersion. It is only through monitoring that cleanup teams can truly determine whether, or not, the dispersant is effective and if termination of its application is necessary. While visual observations of the water's surface might conclude that the dispersant is working, specialized monitoring devices are necessary to determine what activity is taking place below the sea's exterior. In dispersion this where most of the activity can take place, as the oil is being pushed below the surface. In addition to this, environmental conditions (i.e. currents, temperatures, and overall weather patterns) must be taken into account as modeling theoretical spill paths and predicting dilution potential are key aspects of organizing cleanup efforts, more specifically dispersion application methods.

Surface and Subsurface Observations

In surface observations, monitoring can involve both visual and chemical analysis. In terms of appearance, changes should be noticeable shortly after spraying. If no change is visible in the appearance of the oil or there is no reduction in oil coverage, this could be an indication that the dispersant is not working. Also, if the dispersant runs off the oil to create a milky, white plume in the water, this is a clear sign that the dispersant is not reacting with oil as intended (*ITOPF*, 2011). It is equally important to note that, if the oil has spread over a significantly wide area, applying dispersants may not remove enough oil from the water surface to achieve a substantial reduction in pollution damage. With this said, visual observations of effectiveness are limited in poor weather conditions, in waters that contain high sediment load, when dispersing pale-colored oils, or in poor light. For toxicity data, sampling devices with sorbent pads attached can be used to take samples of water on the surface and determine the levels of toxins contained in the water.

For subsurface observations, there are generally two methods used. For simple analysis of specific areas within the water column, a sampling device, which contains sorbents attached to weights, is deployed from a vessel along a cable. Once the device reaches the desired depth, a sample is taken and the sampler is brought back to the surface (*Review/Select Potential Options and Products*, 2003). For a more advanced analysis of the concentration of dispersed oil throughout the water column, fluorometers can be used. One or more fluorometers, which operate based on ultra-violet fluorometry (UVF), are towed behind a sampling vessel, at depths at least 1 metre below the oil slick, measuring variations in oil concentrations (*Use of Dispersants to Treat Oil Spills*, 2011). The effectiveness of the dispersant is represented by a significant increase in the concentration of oil detected by the sensing device, relative to the concentration measured before the dispersant was applied. While the device can be used to observe phenomenon indicative of dispersion, UVF does not provide any quantitative data and should be used with visual analysis in formulating a proper opinion on dispersant effectiveness. **Figure 6**, on the following page, displays readings taken from fluorometers, before and after dispersant was applied.

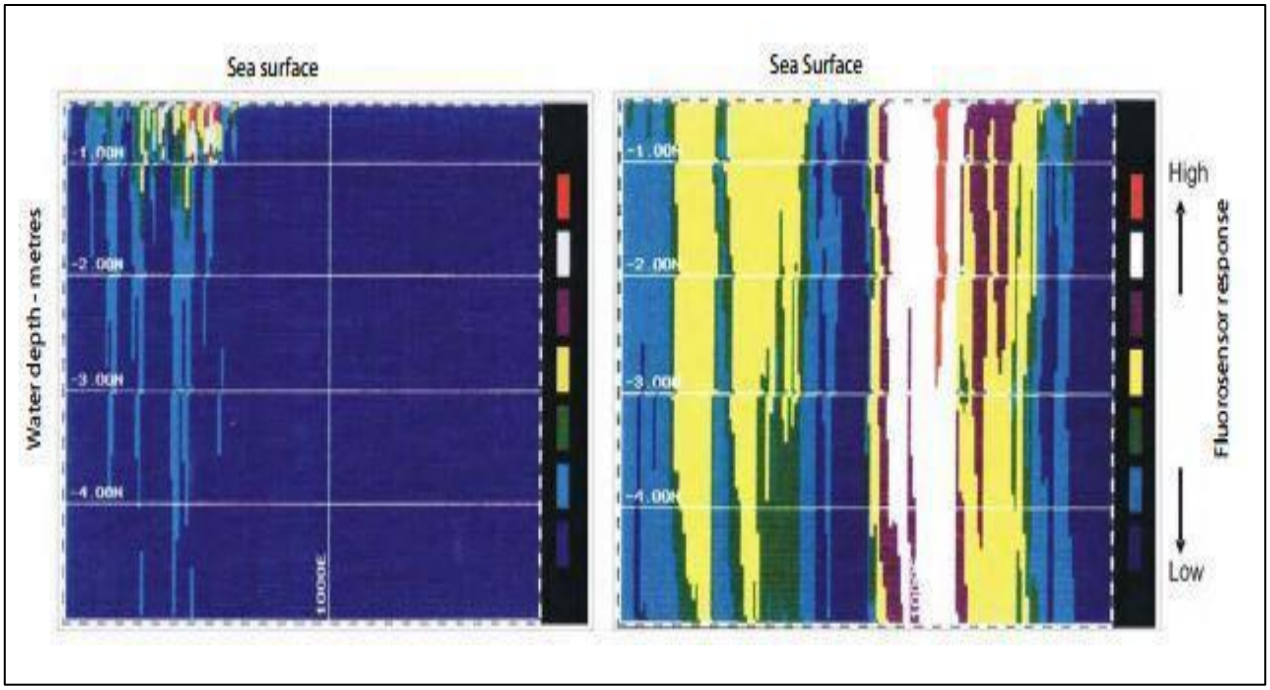

Figure 6. Fluorometer response to oil (Davies, et al., 2001). The reading on the left represents a response to oil 0.5 to 5 metres water depth under a surface slick before dispersant being applied; the reading on the rights represents a few minutes after treatment with dispersant.

Modelling and Predictions

When an oil spill occurs, scientists can use computer models to predict how this oil will travel throughout the waterways. Using known currents and estimated weather patterns, computer models approximate the direction in which the oil will spread (*NOAA Ocean Service Education*, 2008). These models are often referred to as spill trajectory models and can help guide cleanup efforts by showing which locations will most likely require resources, such as dispersants. With this said, once chemical dispersants have been applied, trajectory and weathering analysis will be insufficient in evaluating the effects of subsurface oil (McCay, 2001). In order to effectively evaluate the impact of a spill that is, for the most part, entrained in the water column (due to dispersion), subsurface oil must be explicitly monitored, using a method like UVF, represented on previous page (**Figure 6**).

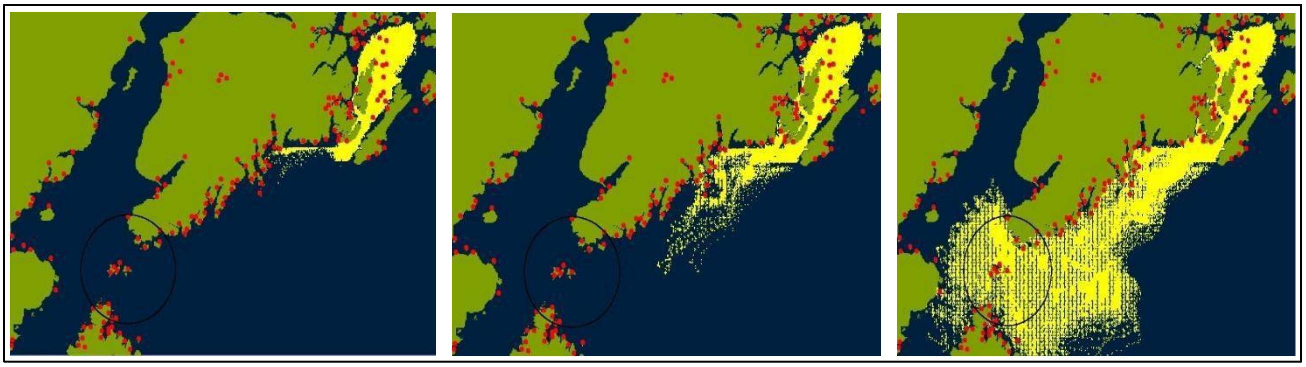

Figure 7. An on-scene spill model developed by the NOAA, during the EVOS (*Centre for Water Science and Engineering*¸ 2007).

Dilution Potential

In combination with spill modeling, predicting dilution potential is a very important factor in deciding whether, or not, dispersants should be used to protect certain areas or resources.

Aspects that require analysis in estimating dilution potential include: estimating peak concentrations and their duration, water depth, oil quantity per unit area, distance between application site and sensitive areas, and the direction and speed of currents (*Use of Dispersants to Treat Oil Spills*, 2011). For the most accurate and thorough predictions, a variety of monitoring and modeling devices are typically used in combination with one another.

IV. FACTORS INFLUENCING EFFECTIVENESS AND EFFICACY OF APPLIED DISPERSANT

While there are a variety of factors that must be thoroughly analyzed prior to applying chemical dispersant on an oil spill, it is equally important to recognize that there is an assortment of physical and chemical influences that can limit effectiveness of the dispersant once it is applied. Although both chemical and physical factors have been reviewed in previous sections, they require independent analysis in reference to applied dispersant, rather than focusing on their influences in decision making processes and application methodology.

Physical Factors

Physical parameters refer to: water temperature, wind velocity, wave height, salinity, and (overall) general sea conditions. While dispersants can work in colder water, they are most effective at warmer temperatures. In frigid conditions, the dispersant and oil can become very viscous, and the dispersant will not react in the oil-water interface as desired (*Dispersing Agents*, 2011). The oil and dispersant will simply be left sitting in the sea independently, opening marine life to more toxins than if the surfactants broke up the oil into smaller droplets.

Under high winds and severe sea conditions (i.e. violent waves), the oil can become submerged, preventing direct contact between the dispersant and the oil; therefore, diminishing dispersant efficacy (*ITOPF*, 2011). Field studies showed that optimum wind speed for applied dispersant is 4-12 m/s or 8-25 knots (*Use of Dispersants to Treat Oil Spills*, 2011). For successful use of dispersants at sea, there should be a minimum amount of wave energy required.

Dispersants are generally designed for saltwater use as most vessel activity and offshore drilling occurs at sea. Most dispersants are manufactured for use in seawater with a salinity of approximately 30-35 parts-per-thousand (ppt) (*Use of Dispersants to Treat Oil Spills*, 2011). When salinity drops below 5-10 ppt, performance of dispersants can decrease significantly; the same effect is seen when salinity rises above 35 ppt (*Use of Dispersants to Treat Oil Spills*, 2011). The reason for reduced efficiency in freshwater is because the surfactants tend to migrate through the oil layer, into the water column, rather than stabilizing at the oil-water interface.
Higher salinity increases the effectiveness of dispersants by deterring migration of surfactant molecules into the water phase, equivalent to a salting-out effect for the surfactant from the saline medium (Weaver, et al., 2006). However, with a salinity of more than 35ppt, the water can become too dense to have the desired effect of decreasing the solubility of dispersants in water and increasing the surfactant available to react and mix with oil (Weaver, et al., 2006).

Chemical Factors

The general behaviour and properties of oil were discussed earlier in section "**I CHEMICAL COMPOSITION AND PROPERTIES"**. In this section, the focus will be specifically on the properties and types of oil that are most suitable for dispersant application. The behaviour of a dispersant is reflective of the characteristics of the oil and the manner in which these properties change due to weathering at sea (*ITOPF*, 2011). Viscosity and pour point are two oil properties that can provide a strong indication of how easily an oil is likely to disperse. The oil composition is also important in terms of its likelihood to form emulsions.

Typically, the effectiveness of a dispersant decreases as oil viscosity increases. Light to medium crude oils are generally considered to be dispersible at most sea temperatures. It is unlikely that heavier oils can successfully be treated with chemical dispersants. In a report submitted by the ITOPF (2011) on "the fate of marine spills", it is stated that most dispersants will be ineffective in treating oils with a kinematic viscosity above 5000 to 10000 centistokes (cSt). The oil spilt from the Exxon Valdez had a kinematic viscosity of approximately 50 cSt (*ITOPF*, 2011).

Following the application of Corexit® 9500, the crude oil spilt in the Gulf of Mexico, due to the DWH blowout, had a kinematic viscosity of 7000 cSt in light brown/reddish emulsions that were observed and 1250 cSt in dark brown emulsions (*Oil Budget Calculator-Deepwater Horizon*, 2010). It is important to remember that the viscosity of spilt oil can greatly increase due to the effects of weathering, forming tough emulsions. With this said, there is a limited amount of time available, following a spill, for the successful application of dispersants; if the application is delayed, the oil can become too viscous to be treated.

Oils with a pour point that is higher than the ambient temperature (i.e. sea temperature) are typically transported heated and, if spilt, the viscosity of the oil will increase drastically, as its temperature is cooled by the water (*ITOPF*, 2011). In some cases, the oil will become semi-solid; therefore, as a general rule, if the oil has a pour point that is close to or higher than the sea temperature, it should be treated as non-dispersible

(*Use of Dispersants to Treat Oil Spills*, 2011). Oils that contain a high pour point, in turn those with a high viscosity, do not disperse easily, both naturally and after the application of chemical dispersants. With a high viscosity, the oil sees a mechanical resistance that prevents small droplets from breaking away from the slick.

When focusing on the composition of the oil itself, some oils are more likely to form water-in-oil emulsions than others. Oils that contain a high asphaltene content (>0.5%) and a nickel/vanadium concentration of greater than 15 parts-per-million (ppm) have a high likelihood of forming emulsions (*ITOPF*, 2011). If the emulsions are unstable, chemical dispersants may be able to break it up the water and liquid oil, later requiring a second application of dispersant.

RESULTS / DATA / ANALYSIS

V. USE OF COREXIT® DISPERSANT

While there are several dispersants authorized by the EPA, it is arguably Corexit® that has received the most media attention over the years, as various analysts claim that the Corexit® product lines, most specifically the 9580, 9500, and 9527 formulas, contain hazardous substances that could significantly harm marine life and other organisms that came in contact with it.

Corexit® 9580

Corexit® 9580 was used in the 1989 EVOS disaster, in which the *Exxon Valdez* oil tanker ran aground in Prince William Sound, Alaska, spilling more than 11 million gallons of crude oil (*Exxon Valdez*, 2013). While Corexit® 9580 is classified as a shoreline cleaner, rather than an on- sea chemical dispersant, it should be noted that this product gained much controversy over its effects on human health. Corexit 9580 was only moderately toxic to early life stages of fish, crustaceans, and mollusks, with a LC50 of 1.6 to 100 ppm (MSDS: Corexit® EC9580A, 2011) and showed promising results in terms of efficiency, with even low dispersion rates (see **Figure 8.**, pg. 23). However, despite workers following recommended safety procedures in terms of handling and application, at the time there were very limited studies done on the long-term affects the cleaner could have to both marine life and human health. According to first-hand accounts, as outlined in *Silence in the Sound: Aftermath of Exxon Valdez Oil Spill* (2010), years later, a large portion of cleanup workers who handled the material now suffer from ailments onset by exposure to the chemical mixture; investigations into such claims are ongoing. Shortly after application processes began, they were discontinued due to unfavorable wave activity limiting the efficiency of the cleaner.

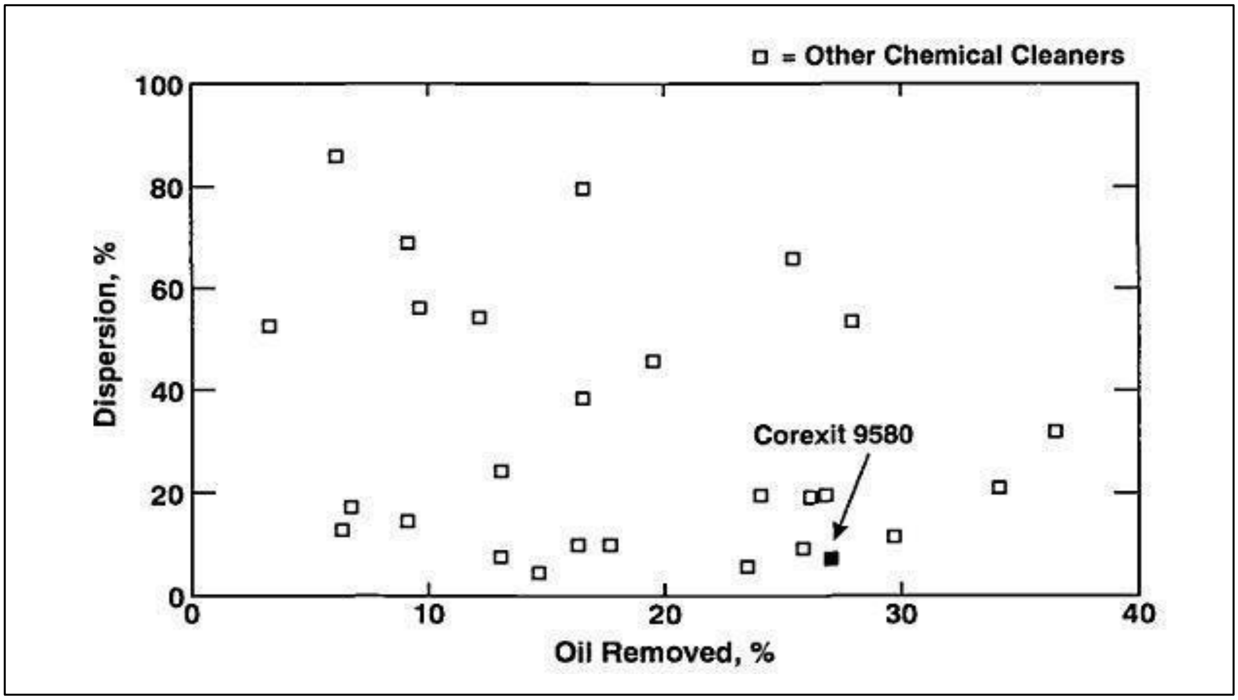

Figure 8. Laboratory Screening Results Show Low Dispersion and High Effectiveness of Corexit® 9580 Beach Cleaner (Lane, 1995).

Corexit® 9500, and Corexit® 9527

Corexit® 9500 and 9527 are dispersants that were used immediately following the Deepwater Horizon (DWH) blowout in the Gulf of Mexico. In the case of the DWH drilling rig explosion, 5 million barrels of oil were leaked into the sea, making it one of the worst environmental disasters in history (Pulster, et al., 2013). The use of the 9500 and 9527 product lines, in the extensive cleanup efforts required with such a large spill, was highly controversial. The application process involved a never-before-seen technique of applying the dispersant directly underwater, rather than on the surface, which typically pushed the effects of the oil below the surface. In addition to this, Corexit® already had a controversial track record with its use in the EVOS. While the underwater technique was thought to be the most sensible, due to the amount of oil below the surface, many were skeptical about the damage the dispersants could cause to populated marine ecosystems. The following table lists the chemical components of the dispersants Corexit® 9500 and Corexit® 9527, as outlined in the toxicology reports required by the EPA for all authorized dispersants.

Components of Corexit® 9500 and 9527

CAS Registry Number	Chemical Name
57-55-6	1,2-Propanediol
111-76-2	Ethanol, 2-butoxy-*
577-11-7	Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.
29911-28-2	2-Propanol, 1-(2-butoxy-1-methylethoxy)-
64742-47-8	Distillates (petroleum), hydrotreated light

Note: This chemical component (Ethanol, 2-butoxy-) is not included in the composition of COREXIT 9500. CAS Registry numbers are in accordance with the American Chemical Society and are used for identification in toxicology analysis of chemical mixtures.

Table 1. EPA report of the chemical components of the dispersants Corexit® 9500 and 9527 (*EPA's List of Authorized Dispersants*, 2013).

According to the results of several toxicity studies, as reported by a variety of health and research institutes, including: the National Oceanic and Atmospheric Administration (NOAA), the United States EPA, and the National Institute for Occupational Safety and Health (NIOSH), many of these chemicals can have an adverse impact on animal health and marine environments. **Table 2**, on the following page, summarizes the studies made by the NOAA, EPA, and NIOSH, in regards to several of the chemicals found in Corexit® 9500 and Corexit® 9527.

Chemical	***Potential Human Health Impacts AND Anmial Studies***
Sorbitan, mono-(9Z)-9-octadecenoate	• Occupational exposure has been recorded to cause contact eczema in one case Animal Studies • Rats fed varying amounts of this compound over a span of 16 weeks experienced liver enlargement and increased kidney weight • The lowest observed adverse effect level (LOAEL) occurred when rats were eating this compound at a rate of 2.5% of their body weight • In tests, rats fed this compound did not experience mortality. Observed effects included depression, decreased respiration, diarrhea for first 72 hours • Reported to be practically nontoxic
Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.	• Exposure may cause chemical pneumonitis (inflammation of lungs and difficulty breathing) and intestinal obstruction • Possible eye, skin, and respiratory tract irritant • Listed as practically non-toxic • Occasional reports of hypersensitivity Animal studies • Adverse reproductive effects have occurred in experimental animals • Effects on development of embryo and fetus have occurred in experimental animals
Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.	• Slightly hazardous in case of ingestion or inhalation Animal studies -limited research on animals
Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)	• Listed as a suspected neurotoxicant • Toxic to blood • Classified as moderately toxic. • Liquid is strong irritant to eye and may irritate skin by removing natural oils. • Ingestion causes diarrhea and intestinal bloating. Animal studies • Oral exposure caused these effects in rats: low body weight (of adults), decreases in maternal weight gain, low birth weight of pups, and malformed fetuses. • Severely damaging to rabbit eyes at 10% concentration. • Mice and rats repeatedly exposed to butanedioic acid showed gastrointestinal problems, reduced weight gain, and death at certain doses.
2-Propanol, 1-(2-butoxy-1-methylethoxy)-	• Listed it as a suspected neurotoxicant. Animal studies • Prolonged exposure to skin may cause drying of the skin, leading to dermatitis • Slightly irritating to eyes

Table 2. Toxicity research findings for chemicals found in Corexit® 9500 and 9527. *Data was summarized from studies referenced in A Small Dose of Toxicology: The Health Effects of Common Chemicals (Gilbert, 2011).*

In relation to the petroleum distillates contained in Corexit® 9500 and Corexit® 9527, the following table lists how these chemicals can negatively impact human and animal health.

Potential effects of: Distillates (petroleum), hydrotreated light
• Confirmed animal carcinogen with unknown relevance to humans • Prolonged inhalation of high concentrations may damage respiratory system • Frequent and prolonged skin contact may cause dermatitis • Exposure by inhalation can cause dizziness, headache, nausea, drowsiness, and unconsciousness • Exposure to the skin can cause dryness • Exposure to the eyes can cause redness

Table 3. Negative effects of distillates (petroleum), hydrotreated light (Gilbert, 2011).

In addition to the potential impacts on animals and humans, some of the chemicals given in **Table 2** can affect marine environments. As outlined in application documents submitted to the EPA by Nalco Energy Services (*Technical Product Bulletin #D-4*, 1994), some of the notable potential marine environment impacts of these chemicals are shown in **Table 4** on the following page.

Chemical	*Potential Marine Environment Impacts*
Sorbitan, mono-(9Z)-9-octadecenoate	- Recorded biodegradation of 62% in 28 days
Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)	- Possibility of absorbing to sediment - Slight acute toxicity to fish
2-Propanol, 1-(2-butoxy-1- methylethoxy)-	- In tests, fish experienced a 50% mortality rate in concentrations of 841 mg/liter of water for 4 days - Aquatic invertebrates did not experience any effects after exposure to a concentration of 1000mg/liter of water for 2 days

Table 4. Potential marine environment impacts of chemicals found in Corexit® 9500 and Corexit® 9527.

Detailed reports and studies on the short-term and long-term of chemical dispersant mixtures, rather than the impacts of individual chemicals outlined earlier, are found in sections "**VII. SHORT-TERM EFFECTS**" and "**VIII. LONG-TERM EFFECTS**".

VI. SHORT-TERM EFFECTS

As stated throughout the report, the use of chemical dispersants on spilt oil has been controversial since it's use was first popularized in the 1960's. Due to the claims that it can have various negative effects on marine life and potentially human health**,** while damaging sensitive habitats such as coral reefs, many feel that dispersant use should be discontinued in North America. When analyzing the short-term effects on different groups of species, it is important to recognize that the risk of damage caused by dispersed oil must be balance against the advantages of removing the spilt oil from the surface of the water. In removing the oil from the surface, dispersants can significantly minimize the risk of sea birds becoming oiled, while protecting shorelines and other sensitive areas from becoming contaminated. Oiled birds can draw a lot of negative media attention as they are typically the first, and most obvious, signs of damage caused immediately following an oil spill. Unfortunately, when oil is removed from the surface by dispersants, it is pushed down into the water column, risking various fish species with increased toxicity of the water. While studies on the long-term effects of dispersant use are limited, there has been a variety of studies done on the potential short-term effects of applying these chemical mixtures to oil spilt at sea.

Algae, Zooplankton, and Microbial Populations

Beginning with a focus on the smaller scale, field studies have shown that dispersed oil can affect algae, zooplankton, and microbial populations, compromising the base of the marine food web (*Using Oil Dispersants on the Sea*, 1989). In field studies conducted by the University of Rhode Island's Maine Ecosystem Research Laboratory, the microbial responses of various microorganisms to Kuwait crude oil (light) dispersed by Corexit® 9527 were effectively analyzed (*Using Oil Dispersants on the Sea*, 1989). Through introducing a premixed mixture of Kuwait crude oil and Corexit® 9527 into a controlled seawater environment, researchers were able to study the responses of plant, algae, and plankton populations to dispersed oil. In general, the results showed that dispersed oil supported increased microbial growth, particularly on plant and algae surface, while changing the composition of phytoplankton populations (*Using Oil Dispersants on the Sea*, 1989). It was also observed that there was a significant reduction in zooplankton, and sometimes phytoplankton, populations, which would affect bottom feeders who rely on these populations for food. After a 2-week period, researchers noted a slight increase in the population of the formerly reduced species (*Using Oil Dispersants on the Sea*, 1989).

Fish

In deciding whether, or not, to use dispersant, typically the primary factor in choosing is how it will affect fish populations. When analyzing the acute toxicity (multiple exposures in a short period of time) of oil to marine fish larvae, researchers at the University of Aberdeen concluded that the aromatic content of the dispersant was the main factor in influencing the toxicity to the larvae of several species, including: haddock, herring, lemon sole, pilchard, plaice, and sole (Wilson, 1997). Generally, with a higher aromatic content, the substance will mix more easily with oil and water. Newer dispersants (i.e. Corexit® 9500 and 9527) have much lower toxicities, with ageing of these dispersants leading to further decreases in toxicity, which is likely a result of the loss of aromatic compounds from the solution (Wilson, 1997). It is noted in the University of Aberdeen study that, for all dispersants, differences of susceptibility between species were less than differences at different ages within a species. The larvae of all species studied showed a similar susceptibility when newly hatched, as susceptibility increased throughout early development (Wilson, 1997). In the study, researchers observed that the transition period from yolk reserves (early development feeding) to an external food supply was the most important, as once the larvae had established feeding, resistance increased until metamorphosis (physical development). The dispersants behaved as a physical toxin causing a reversible narcosis; therefore, limiting development and hindering spawning periods (Wilson, 1997). Similar behaviour was seen in the analysis of plankton and fish populations in the Prince William Sound and along the Alaskan coast, following the EVOS (*Centre for Biological Diversity*, 2012).

When looking at adult fish, unfortunately, there is a limited number of reliable studies in comparing how the effects of dispersed oil differ from untreated oil (*Using Oil Dispersants on the Sea*, 1989). In a combined laboratory-field study of salmon, conducted by the EPA, the effects of dispersed oil, as compared to untreated oil, on adult fish were examined (*Using Oil Dispersants on the Sea*, 1989). Because of their highly developed chemical sense, it was believed that these fish would be adequate test subjects in whether, or not, their senses would be disturbed by low concentration of chemically dispersed oil. In the study, 215 adult Chinook salmon were caught in a freshwater pond, anesthetized, tagged, and divided into four tanks (**Table 5**, shown on the following page).

Tank 1	Tank 2	Tank 3	Tank 4
an untreated control group	a tank with untreated Prudhoe Bay crude oil as a 0.5 mm thick slick	a tank containing 105 ppm of chemically dispersed crude oil (10:1 oil to dispersant)	a tank containing 10.5 ppm of freshwater chemical dispersant

Table 5. EPA study outline on effects of dispersed oil and untreated oil on Chinook salmon (*Using Oil Dispersants on the Sea*, 1989).

After a 1-hr exposure to the varying environments, the salmon were removed from the exposure tanks and held overnight in a raceway. The following morning, the salmon were taken 9km downstream and released. Out of the 215 salmon that were released, 154 (approximately 72%) returned to the pond from which they were originally caught, before being brought down stream (*Using Oil Dispersants on the Sea*, 1989). These results showed that there was little effect on homing success when salmon saw short-term exposure to either type of oil (i.e. dispersed Prudhoe Bay crude oil and untreated oil); the salmon that did not return were attributed to fishing activity near the release point. Homing was considered an adequate area of study as the chemical senses of salmon are essential in this process. The olfactory systems of the salmon, which control sense of smell, were not impaired enough, after short-term exposure to the dispersed oil, to interfere with homing (*Using Oil Dispersants on the Sea*, 1989). It was noted in the study that, while salmon may avoid oil in the water column under uncontrolled conditions, when exposure was forced upon the species, chemically dispersed oil at high concentrations did not prevent or delay homing.

Corals

There is currently legislation in place in North America and areas of Europe that prevent petroleum companies from using dispersants in areas near coral reefs (*Dispersing Agents*¸ 2011). Scientists have proven that dispersed oil can be very toxic to corals and leading researchers believe there should be a world-wide ban on its use in areas with coral. According to the Center for Biological Diversity (2012), Corexit® 9527, which as stated earlier was used in the BP DWH spill, has been shown to prevent fertilization of mature eggs and hinder the development of young life stages of reef-building corals.

Birds

While oil slicks and build-up oil along shorelines can be dangerous to bird populations, ingestion and exposure to dispersed oil can be just as harmful. Studies of Corexit® 9527 and its use in the EVOS found that, similar to exposure to untreated oil, when seabirds came in contact with dispersed oil their feathers were damaged affecting their insulating properties, making them susceptible to hypothermia and death (*Center for Biological Diversity*, 2012). Even for birds that were professionally treated and cleaned, minimal exposure could cause death. The same studies found that dispersed oil can have toxic effects on bird eggs, passed on by exposed mother birds, that are worse than that from untreated oil.

Human Health

Studies on the effects of dispersants and dispersed oil on human health are very limited. While there have been many claims from cleanup personnel and other oil workers, as discussed in section "**III. USE OF COREXIT® DISPERSANT**", there has been little or no scientific data or monitoring to confirm this. With this said, some of the ingredients found in chemical dispersants are known to have toxic effects on humans. According to the EPA, 2-Butoxyethanol, a chemical found in Corexit® 9527 (see page 7 for chemical components of Corexit® dispersants), may "cause injury to red blood cells (hemolysis), kidney or the liver, with repeated or excess exposure" (*MSDS: Corexit® EC9580A*, 2011). What "excess" exposure for humans entails is not stated in the MSDS; however, it would be safe to assume that with close to 1 million gallons of dispersant being applied to the surface in the DWH spill, workers would be subject to some level of exposure.

VII. LONG-TERM EFFECTS

One of the main reasons that the use of chemical dispersants on spilt oil has been so controversial, since it first began, is that research on its long-term effects is extremely limited. Even the EPA has been quoted as stating that "the long-term effect [of dispersant] on aquatic life are unknown", not to mention that research on the long-term effects of exposure to humans is virtually non-existent (*Center for Biological Diversity*, 2012). Research on the long-term impacts of dispersed oil on marine life has not been adequately tested; however, BP, in accordance with the EPA, has set in place long-term monitoring systems, in an attempt to analyze the long-term effects of dispersed oil in the DWH case, and bring about more legitimate conclusions on chemical dispersants (*Dispersing Agents*, 2011). It is not fair to say there has been no research done on long-term impacts, as studies done on dispersed oil in shallow environments, particularly around shorelines, have shown that long-term exposure can be detrimental to plant life and low water living organisms. However, it is in open sea environments that research is really needed, as dispersants are no longer authorized around shorelines. Perhaps with the extended monitoring and analysis planned for the spill in the Gulf of Mexico, researchers can formulate a better understanding of the long-term impacts of chemical dispersants and dispersed oil.

CONCLUSION

Due to the known toxic effects of several of the chemical found in oil dispersants, such as Corexit® 9500 and 9527, which are authorized under the NCP product schedule, dispersants should only be considered when mechanical means, such as skimmers and oil-water separators, are not sufficient. If chemical dispersants are being considered in oil spill cleanup efforts at sea, careful consideration must be given to several factors, such as: weathering, oil type, dispersant potential, wave activity, application processes, birds and marine life, and a variety of other environmental conditions.

There is limited research, scientific data and overall understanding of the potential long-term effects of dispersant use to confirm if dispersed oil is less, or more, dangerous than untreated oil due to the break-down products generated. With this said, there is sufficient evidence to support that dispersants use is not effective on oil accumulated near shorelines or in shallow-water environments. For cases where oil dispersants are used, acting companies should be expected to perform long-term monitoring on water quality, local habitat, and marine life. Overall, chemical dispersants should be viewed as a last resort in terms of cleanup processes as there is simply not enough known about their true impact on marine environments and the health of a variety of species.

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