Surface and Subsurface Application of Chemical Dispersants and Associated Ecosystem Impacts

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This Master's Project

SURFACE AND SUBSURFACE APPLICATION OF CHEMICAL DISPERSCANTS AND ASSOCIATED ECOSYSTEM IMPACTS

by

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is submitted in partial fulfillment of the requirements
for the degree of:

Master of Science

in

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Chemical dispersants are applied to spilled oil in marine environments when other, less controversial, methods are not adequate for the incident. They are considered to be a response method as opposed to a direct cleanup method, with the intended goals of reducing risk of exposure to sensitive shorelines, reducing environmental injury to surface-dwelling sea birds and marine mammals, and facilitating the biodegradation of spilled oil into the water column.

For this research, both surface and subsurface application of dispersants were evaluated in terms of oil characteristics and volume, and oceanic and atmospheric conditions. More data exists to support the effectiveness of chemical dispersant application at surface water oil slicks as opposed to subsurface plumes. However, since Deepwater Horizon in 2010, there have been several hundred scientific research papers published to study subsurface application of oil spill dispersants.

While the efficacy, ecosystem impacts, and ultimate fate of chemical dispersants and dispersed oil generates conflicting opinions in the scientific community, there are measures that could be taken in order to minimize potential impacts. Research that accounts for variable conditions and ecosystems could be initiated, simulating field conditions in laboratory settings, processing data from Deepwater Horizon, and utilizing current response and monitoring protocols.
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<td>Total Petroleum Hydrocarbons</td>
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CHAPTER 1 – INTRODUCTION

The United States’ (U.S.) dependence on petroleum refined from crude oil as a primary energy resource has been linked to various ecological issues within the natural environment. In 2013, the largest allocation of American consumption of refined petroleum represented the fuels for transportation, including gasoline and jet fuel (54%), and fuel oils that support electricity and heating generation (20%) (EIA, 2015). Other commonly used products or resources derived from refining petroleum include asphalt and road oil, natural gas liquids, liquefied refinery gases, lubricants, and feedstocks that produce chemicals, plastics, and other synthetic materials used in virtually everything we use today (EIA, 2015). Throughout its entire life-cycle, crude oil and petroleum distillates have had adverse consequences that stemmed from extraction, refinement, transportation, combustion, and disposal (Silva et al., 2014). However, the potential stage in its life-cycle that can have a catastrophic and unpredictable outcome is that of accidental spill, discharge, or explosion – which can occur in any and all of the other stages.

This chapter provides an overview of petroleum releases to the marine environment and identifies both traditional oil spill response methods and applied response technologies. Of the applied response technologies presented, the use of chemical dispersants is most controversial, as it minimizes surface ecosystem impacts while potentially maximizing subsurface ecosystem impacts. Using case studies, this research discusses specifics of surface versus subsurface dispersant application, identifies associated ecosystem impacts from the two application methods, and presents management recommendations for future dispersant use.

1.1 Releases to Marine Environment

Inspired by the Industrial Revolution in the early nineteenth century, innovations in transportation, manufacturing, and energy consumption brought about monumental changes to the U.S. industrial machine (Library of Congress, 2007). The popularity of using petroleum as a primary energy source resulted in increased oil commerce and transportation by railcar, ocean tanker, and barge (Library of Congress, 2007). An unfortunate byproduct of this increased oil transportation was the incidents that resulted in accidental discharge. Although countless releases of this nature have occurred since long distance trade began, it was not until the creation of the U.S. Environmental Protection Agency (USEPA) in 1970 that the U.S. government
implemented regulatory powers to mitigate response to such environmental disasters (Lewis, 1988). Despite increased awareness and stricter regulations, approximately 5.65 million tons of crude oil have entered the global marine environment resulting from tanker discharges between 1970 and 2009 (Tamis et al., 2012).

One of the concerns of the discharge of crude oil into the marine environment is the exposure of marine organisms to total petroleum hydrocarbons (TPH), which are comprised of hundreds of chemical compounds that can react with water, air, and sediment in different ways (ATSDR, 1999). If discharged at the water’s surface, these fractions can exist at the surface where they form slicks or films and release additional hydrocarbon fractions through evaporation, whereas if discharged from a point below the surface they can form a plume of petroleum derivative contaminant and store in sediments (Sammarco et al., 2013). In all cases, it is also possible that the various fractions of TPH will react with or accumulate in marine organisms and sediment, if it does not disperse in the water. Since the transport and ultimate fate of the released oil has different reactions within surface water, water column, shoreline, sediment, and air, the following section will summarize the various processes in which environmental remediation can occur naturally or as a tactical emergency response.

1.2 Potential Oil Spill Response Methods

When a high-volume spill occurs in an open water aquatic environment, the foremost course of action is to contain and manage the oil that has already been discharged or continues to discharge. The need for an immediate response is the consequence of how spilled oil behaves in the marine environment. When discharged into water, oil can experience several biological, physical, and chemical transformations that influence its path and transport (Gong et al., 2014a). These processes include adsorption, biodegradation, dispersion, dissolution, emulsification, evaporation, photo-oxidation, sedimentation, and spreading, as shown below in Figure 1 (Gong et al., 2014a).
Due to the complexities involved with oil transport in the marine environment, incident response plans and methods must be adapted to meet the needs and conditions of the particular environment. There are several methods that have proven to be successful at oil spill remediation in past incidents, when used individually or in a combination. These methods include mechanical containment, in-situ burning (ISB), chemical dispersion, and natural dispersion (no response) (Kinner and Ballestero, 2012). Determining which response tactic to employ depends on various factors such as ecosystem, season, present oceanic and atmospheric mixing energy, type of oil, and socioeconomic or political conditions of the region (Kinner and Ballestero, 2012). The aforementioned environmental factors can influence how oil is transported in water, which then governs how to effectively manage the spill. If there is little mixing energy from waves, wind, or other related turbulence, on-water skimming is typically the first remediation strategy (Chang et al., 2014). The reason is that containment methods such as booms are used to capture and enclose oil at the water surface where it floats, so removal via
mechanical recovery or ISB can occur in a concentrated location without use of potentially toxic chemicals (Chang et al., 2014).

If mechanical recovery is not effective, the spilled oil is dispersible, and conditions can potentially reduce environmental impacts, then applying chemical dispersants is the next response method for large-scale oil spills. The anticipated effects from applying chemical dispersants to oil in water are reducing the exposure of hazardous threats to marine organisms, and responders at the water surface, preventing the oil from migrating towards sensitive coastal ecosystems, and accelerating the natural dispersion of oil into the water column (Tamis et al., 2012). Potential implications of chemical dispersant use will be discussed more in-depth in later sections of this paper. The next section outlines past cases where dispersants were used or considered for use for large-scale oil spills that resulted in significant impacts on their respective marine ecosystems.

1.3 Dispersant Case Study Overview

Most spills occur in the open ocean from tankers, barges, or pipelines and preventing the oil discharge from traveling to reach vulnerable ecosystems near the shoreline is prioritized (Chang et al., 2014). In order to achieve this result in ideal conditions, chemical dispersants are applied to surface waters in the marine ecosystem so that the oil will be forced from the surface into the water column (Gong et al., 2014b). The intended impact of the chemicals onto the oil is to reduce the interfacial tension between oil and water, which breaks down large areas of slick into smaller, dispersible droplets that distribute into the water column (Chang et al., 2014). The case studies mentioned below are discussed in chronological order.

1.3.1 T/V Exxon Valdez (1989)

The Exxon-Valdez oil spill took place on March 24th, 1989 in Prince William Sound, located within the Gulf of Alaska (Boufadel and Bobo, 2011). The single hulled tanker vessel T/V Exxon Valdez struck Bligh Reef while maneuvering in dangerous waters, discharging approximately 250,000 barrels or 11,000,000 gallons of Alaska North Slope crude oil with an American Petroleum Institute (API) gravity of 29.8 into the ocean (NRC, 2005; Boufadel and Bobo, 2011). Although the spill occurred only 1.8 kilometers (km) from the western shores of Bligh Island, it remained relatively close to the accident area until a harsh winter storm generated
mixing conditions that caused the slick to spread to approximately 2,000 km of rocky intertidal shorelines (Boufadel and Bobo, 2011). This spreading and mixing resulted in significant impacts on the effectiveness of chemical dispersant applications and caused lasting damage to resources within the coastal marine environment.

1.3.2 M/V Blue Master (1999)

On August 27th, 1999, the merchant vessel M/V Blue Master was charted for a course to New Orleans, Louisiana and collided with the fishing vessel F/V Captain, who veered off course while fishing in waters near the vicinity of the Blue Master (Kaser et al., 2001). The collision occurred approximately 55 km south of Galveston, Texas, and resulted in the discharge of 1,000 barrels or 4,200 gallons of Intermediate Fuel Oil (IFO) 180 that leaked through a one square foot hole in the deep oil tank (Kaser et al., 2001). Although several conditions did not exist to meet parameters for the Pre-Approved Dispersant Use Manual, the chosen response tactic for removing IFO 180 spill was to apply chemical dispersant Corexit 9500 to the water’s surface by aircraft (Kaser et al., 2001). This decision to apply Corexit 9500 to disperse the IFO 180 during the spill minimized negative impacts to the marine environment, based on no reports of injured wildlife and a total of 1.5 barrels of oil reaching the shoreline one week later in the form of tarballs (Kaser et al., 2001).

1.3.3 Poseidon Pipeline (2000)

On January 21st, 2000, a 24 inch diameter oil pipeline was struck by an 8.8 metric ton anchor, dragging and displacing the pipeline approximately 204 meters (m) from where it formerly stood, and resulted in the discharge of oil from three different locations along the pipeline (Stoermer et al., 2001). Despite the ability of the pipeline to transport 500,000 barrels of crude oil every day, the amount of discharge from the Poseidon Pipeline was approximately 2,000 barrels or 84,000 gallons of sweet Louisiana crude oil with an API gravity of 31.5 into the Gulf of Mexico, 105 km south of Houma, Louisiana (Stoermer et al., 2001; NRC, 2005). The application of the dispersant Corexit 9527 was considered successful by the United States Coast Guard (USCG) due to the minimal remainder of visible oil slick and minimal impacts to marine wildlife.
1.3.4 Eugene Island Pipeline (2009)

On July 25th, 2009, an alarm had notified Royal Dutch Shell of a drop in pressure somewhere along their 20 inch diameter, 18 m deep, and 173,000 barrel-per-day (BPD) capacity pipeline (NOAA, 2010). USCG divers found a crack in the pipeline that was located approximately 48 km offshore the Louisiana Coastline and 97 km southwest of Houma, Louisiana (Fletcher, 2014). It was widely speculated that this crack was the result of aging infrastructure, staining, and corrosion of the pipeline system (Fletcher, 2014). Shell had estimated that approximately 1,500 barrels or 63,000 gallons of Eugene Island grade crude oil with an API gravity of 33.7 was discharged into the Gulf of Mexico (Fletcher, 2014). The Emergency Response Division (ERD) of the National Oceanic and Atmospheric Administration (NOAA) responded to this incident by identifying at-risk resources, providing trajectories for flight crews during aerial application of chemical dispersants, and conducting monitoring for dispersant efficacy when they were applied to the water’s surface (NOAA, 2010). Even though the damaged section of the pipeline was shut down following the leak’s discovery, repairs did not commence until five days after the spill occurred, resulting in a visible oil sheen that spanned over 207 km² (Oil Spill Intelligence Report, 2009). Although there is little information available regarding the logistics or efficacy of dispersant application during this spill and communication gaps had occurred between response teams and the Incident Command Post (ICP), the USCG Gulf Strike Team (GST) had kept logs of the incident response pertaining to dispersant application (Fletcher, 2014).

1.3.5 Deepwater Horizon (2010)

Considered the second largest oil spill of all time, the Deepwater Horizon (DWH) British Petroleum (BP) oil rig explosion occurred on April 20th, 2010, and in terms of oil released into the marine environment, dwarfed the Exxon Valdez spill (Wilson, 2014). Unlike all past oil spill incidents, damage to wellheads occurred during deep-sea oil extraction that resulted in a subsurface leak approximately 1 mile (mi) below the water’s surface. A fire and explosion on the DWH rig caused the Macondo 252 well (MC252) to explode, discharging nearly 60,000 barrels or 2,500,000 gallons of API gravity 37.2 Macondo crude oil (ENT-052210-178) per day, and a total of approximately 4,900,000 million barrels or 206,000,000 gallons directly from the
wellhead into the Gulf of Mexico (Tamis et al., 2012). The size, scale, and amount of crude oil that had discharged from MC252 forced responders to take revolutionary courses of action to combat the continuously surging leak. Chemical dispersants (mostly Corexit 9500) were tested and eventually applied at the subsurface wellhead (Spier et al., 2013). For the first time in history dispersants were applied to treat an ongoing leak in subsurface water, directly at MC252, 1,500 m below the DWH platform (Spier et al., 2013).

1.4 Research Summary

Crude oil remains a vital source of energy but still poses potentially devastating risks from spills to marine ecosystems, as well as from associated response methods. This research assesses the differences in application processes of chemical dispersants in surface and subsurface marine waters during oil spills, while weighing environmental tradeoffs in each ecosystem. Chapter 2 examines chemical dispersants, focusing on their characteristics and circumstances in which they are being or have already been used for mitigation purposes. Chapters 3 and 4 provide overviews of the application process of chemical dispersants in surface and subsurface waters, respectively, and conditions that are present during each situation. Following overviews of the application processes, Chapter 5 discusses ecosystem impacts associated with surface and subsurface application, which focus on large-scale implications and toxicity to trophic levels within the impacted ecosystems. Chapters 6 and 7 summarize research conclusions and suggest several management recommendations.
CHAPTER 2 – CHEMICAL DISPERSANTS

Chemical dispersants are composed of solvents, surfactants, and other additives that are considered to be valuable tools to minimize environmental injuries to surface water organisms caused by oil spills in marine ecosystems (NRC, 2005). There are various grades and volumes of dispersants that can be applied during spills whose use is dependent on several factors. These factors include the time window in which the oil was initially spilled, environmental conditions of the impact area, grade of oil intended for dispersal, and any pre-approved application schemes that may exist in that region (Tamis et al., 2012). Dispersants are applied directly to the impacted area typically by aircraft, marine vessel, or pump either at the water’s surface or into the water column in order to: 1) limit the outflow of oil from the spill source, 2) augment the mechanical removal process, 3) restrict further spreading of oil, 4) accelerate natural dispersion of oil droplets into the water column, and 5) reduce impacts of oil to seabirds and marine mammals (Tamis et al., 2012).

According to the USEPA’s Report on the Use of Chemical Dispersants for Marine Oil Spills (1993), the application of chemical dispersants to combat oil spills is categorized as a response method as opposed to a direct cleanup method. The reason for this distinction is because chemical dispersants do not actually remove the oil from the marine environment, but instead reduce the interfacial surface tension between water and oil so that the oil compounds break down into smaller droplets [< 20 micrometers (µm)] that can mix and dilute into the water column (USEPA, 1993). Furthermore, the decision to use chemical dispersants comes only if a mechanical response is deemed insufficient, as illustrated in Figure 2.
2.1 History of Chemical Dispersant Use

Although this research focuses primarily on chemical dispersant application for oil spill events in the U.S., it is noteworthy to discuss the response tactics used during the 1967 Torrey Canyon tanker spill off the coast of England as a historical event that set the stage for the evolution of chemical dispersants, as well as the corresponding regulatory framework.

2.1.1 Torrey Canyon Tanker Spill (1967)

After approximately 1,000,000 barrels or 42,000,000 gallons of Kuwait crude oil were discharged from the Torrey Canyon, approximately 10,000 barrels or 420,000 gallons of various chemical detergents or degreasers were applied to the water and shoreline in an unprecedented attempt to disperse the oil (NRC, 1989).
This first generation of chemical “dispersants” used in the Torrey Canyon tanker spill were essentially aromatic hydrocarbon-based degreasing agents that were produced to clean tanker compartment holds, bilges, and engine rooms (NRC, 1989). The toxicity of these detergents to the marine ecosystem and the inefficacy to disperse the oil off the English Coast became evident during investigations after the two week period in which the chemicals were applied. Although ninety percent of the less dense surfactants evaporated within one hundred hours, the denser aromatic hydrocarbon and alkylphenol surfactant based composition of the degreasing solvents did not evaporate or dissolve into the seawater (NRC, 1989). These compounds instead emulsified to form stable detergent: oil bonds with a relationship showing the more toxic the dispersant, the more stable the emulsion.

The enhanced toxicity of the oil constituents and negatively synergistic reactions of degreasing solvents with crude oil resulted in widespread mortalities in marine mammals, seabirds, shellfish, algae, and other intertidal organisms (Franklin and Warner, 2011). The chemicals used during the disastrous response efforts of the Torrey Canyon oil spill caused more damage to the marine environment than the spill itself (Kinner and Ballestero, 2012). This deleterious outcome has caused a sentiment of disapproval of chemical dispersant use among the general public of industrialized nations, and the perception is that future dispersant use would have similar adverse environmental effects as it did in the Torrey Canyon spill (Kinner and Ballestero, 2012).

Using chemical dispersants as a response method during the Torrey Canyon spill not only left a lasting and undesirable impression, but raised many questions regarding their environmental impact that have persisted to this day. The Torrey Canyon tanker spill was a signature event that caused Europe, Canada, and the U.S. to endorse groundbreaking research and sponsor programs that would test chemical dispersant efficacy, author guidelines for regional application, and develop the second and third generations of chemical dispersants (ITOPF, 2011). In addition to promoting research for more effective and less destructive chemical dispersant application, this time period during the late 1960s – early 1970s was critical for environmental protection in the U.S., due to the creation of legislation that would lay the foundation for government to start enforcing laws of compliance, accountability, prevention, and response (Franklin and Warner, 2011).
2.2 Regulatory Framework

Regulatory powers and agencies have evolved over the decades to prevent large-scale disasters such as oil spills and control the damage inflicted to the environment when they occur. Interestingly enough, history has shown that much of this evolution has occurred as a direct result of lessons learned – or in other words, after a catastrophe like an oil spill has already taken its toll and exposed the gaps in response strategies for policy-makers to fix. This section provides a summary of several U.S. laws and regulations that have been through this evolution process, and focus on addressing risks of hazardous substance discharge into the environment and selection of response methods that can minimize their impact. A number of these regulations address the use of dispersants for oil spill response.

2.2.1 Clean Water Act

The Federal Water Pollution Control Act of 1948 was the cornerstone of regulations that manage the discharge of various pollutants and establish surface quality standards for all navigable waters of the U.S. (USEPA, 1993). When sweeping amendments came to environmental regulations in 1972, one of the main additions to what is currently referred to as the Clean Water Act (CWA) was imposing a National Oil and Hazardous Substances Pollution Contingency Plan (NCP), which focused on prevention and response to potential future releases of oil and other hazardous substances (USEPA, 2014a). The first NCP was established in 1968 in response to the Torrey Canyon tanker spill and was also the first comprehensive incident response system that included accident reporting, spill containment, spill cleanup, and the designations for response headquarters and national or regional reaction teams (USEPA, 2014a). In 1970, just three years after Torrey Canyon, the U.S. Congress amended the CWA to adopt a “trust but verify” approach towards the use of chemical dispersants (Franklin and Warner, 2011).

2.2.2 National Oil and Hazardous Substances Pollution Contingency Plan

This new approach for requiring an NCP directed the USEPA to coordinate with individual states to identify “dispersants and other chemicals” to be approved for use in response efforts, identify the navigable waters where these dispersants and other chemicals could be applied, and then define the quantities of the dispersants or other chemicals that would be used in such waters (Franklin and Warner, 2011). Efforts to oversee the selection process of dispersants...
to be used in the National Response System (NRS) were increased in 1975 when the USEPA enacted regulations that required data specifications, review standards, and listing procedures for substances to be considered for placement on the dispersant list (USEPA, 2014a). It would not be until 1982 that the USEPA would place all proposed substances to be used in hazardous spill response on a centralized list known as the NCP Product Schedule, based on their composition, chemistry, physical properties, efficacy, and acute toxicology to the natural environment (Franklin and Warner, 2011; and 40 C.F.R. §300.910).

2.2.3 Oil Pollution Act of 1990

In response to the Exxon Valdez tanker spill in 1989, the U.S. Congress passed the Oil Pollution Act of 1990 (OPA90), which addressed inadequacies and faults in the existing regulatory framework for hazardous spill response (Franklin and Warner, 2011). Because chemical dispersants were not a positive factor in the Exxon Valdez spill response due to their unobtainability, the passage of OPA90 essentially increased federal powers to oversee the maintenance of a national, regional, and area contingency plans and imposed accountability for corporations as well as federal, state, and local governments to develop contingency plans that could be used for response to worst-case spill scenarios (Franklin and Warner, 2011). These powers were amended by the USEPA further in 1994 to increase dispersant regulations, however, there were no amendments to the dispersant listing process on the NCP Product Schedule and the process remains similar to this day (Franklin and Warner, 2011; and 40 C.F.R. §300.905). As of December 2014, nineteen dispersants are listed on the NCP Product Schedule of the USEPA as pre-approved for hazardous spill response, and are identified by class and type in the section below (USEPA, 2014b).

2.2.4 Special Monitoring of Applied Response Technologies

The seemingly increasing number of oil spill occurrences and the constant game of catch-up that responders and policy-makers played in effectively managing spills brought about additional reforms and guidelines in 1997, when the USCG, NOAA, USEPA, and Centers for Disease Control and Prevention (CDC) convened to establish the Special Monitoring of Applied Response Technologies (SMART) document (Fletcher, 2014). One of the primary goals of SMART protocols and methodologies is to monitor the efficacy of response technologies used
when applying chemical dispersants during oil spills into marine environments (Bejarano et al., 2013). Following various oil spill incidents which inspired SMART protocols to evolve came the 2006 SMART Protocol, which currently functions as the chief guidance document for SMART (Fletcher, 2014).

Objectives of the 2006 SMART Protocol specify situations in which it shall and shall not apply, and provide a framework for a three-tiered monitoring program for the efficacy of oil spill dispersant operations (Fletcher, 2014). The 2006 SMART Protocol was tailored to be general enough so that addenda pertaining to future and more detailed guidance could be added without complete overhaul of the document. There are several standardized supplemental documents and forms that exist within SMART in order to remain consistent and assist response personnel, as listed in Table 1 below.

Table 1. SMART Supplemental Attachments to Assist Response Personnel During Monitoring of Chemical Dispersant Operations (Fletcher, 2014).

<table>
<thead>
<tr>
<th>Monitoring Dispersant Operations:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roles and Responsibilities</td>
</tr>
<tr>
<td>Command, Control, and Data Flow</td>
</tr>
<tr>
<td>Dispersant Observation General Guidelines</td>
</tr>
<tr>
<td>Dispersant Observation Training Outline</td>
</tr>
<tr>
<td>Dispersant Observation Checklist</td>
</tr>
<tr>
<td>Dispersant Observation Pre-Flight List</td>
</tr>
<tr>
<td>Dispersant Observation Reporting Form</td>
</tr>
<tr>
<td>Fluorometry Monitoring Training Outline</td>
</tr>
<tr>
<td>Dispersant Monitoring Job Aid Checklist</td>
</tr>
<tr>
<td>Dispersant Monitoring Performance Guidelines</td>
</tr>
<tr>
<td>Dispersant Monitoring Field Guidelines</td>
</tr>
<tr>
<td>Dispersant Monitoring Water Sampling</td>
</tr>
<tr>
<td>Dispersant Monitoring Recorder Form</td>
</tr>
</tbody>
</table>
The three-tiered monitoring system is defined as follows: Tier I requires a trained observer from response personnel to conduct visual observations of the impacted area and prepare reports for Incident Commanders, Tier II is the enhanced response to Tier I with the addition of using real-time oil detection and water sampling instruments to record data at single water depths, and Tier III is where data is collected regarding oil transport and dispersion into the water column (Fletcher, 2014). Tier III contains an expanded monitoring procedure that consists of using real-time oil detection and water sampling instruments to record data at multiple water depths (Fletcher, 2014). Several parameters that are measured from water sampling during Tier III include water temperature, conductivity, dissolved oxygen content, pH, and turbidity (Fletcher, 2014).

2.3 Chemical Dispersant Types

The grade and type of chemicals used to disperse spilled oil in water has changed periodically since the Torrey Canyon tanker spill, when toxic degreasing agents containing aromatic hydrocarbons and alkylphenol surfactants caused widespread unintended damages to the marine environment off the English Coast (NRC, 1989). In the decades since the establishment of the NCP Product Schedule, various dispersants have been listed, relisted, and removed based on evaluations from laboratory research and toxicity testing presented to the USEPA (USEPA, 2014b). The key components of the nineteen chemical dispersants that are currently listed on the USEPA NCP Product Schedule contain one or more surfactants (NRC, 1989). These molecules contain both water-soluble or hydrophilic and oil-soluble or lipophilic compounds, as well as a solvent that can reduce the oil’s viscosity and facilitate its dispersal (NRC, 1989). The most well-known chemical dispersants currently listed on the USEPA NCP Product Schedule are Corexit 9500A (formerly Corexit 9500) and Corexit EC9527 (formerly Corexit 9527), due to their use in the oil spill events discussed in this paper, except Torrey Canyon.

2.3.1 Physical Chemistry of Dispersants

Modern chemical dispersants are comprised of a mixture of solvents, additives, and surfactants or surface-active agents that reduce oil-water interfacial tension (NRC, 2005). Interfacial tension is defined as the change in free energy that occurs from change in the contact
area at the interface between two immiscible phases of matter (NRC, 2005). These phases include solid-to-liquid, liquid-to-liquid, and liquid-to-gas (NRC, 2005). These reactions can also be described by the term surface tension, which is generally used interchangeably with interfacial tension even though surface tension requires one of the reactionary phases to involve a gas (Lyklema, 2000).

2.3.1.1 Solvents

Solvents are categorized into three classes of use such that they minimize toxicity, reduce viscosity, and increase dispersant solubility in the oil that is being dispersed (USEPA, 1993). These classes consist of water, water-miscible hydroxy compounds, and hydrocarbons (NRC, 1989). Aqueous or water-based solvents primarily facilitate the dissolution of surfactants and additives into a homogenous mixture of dispersant (NRC, 2005). The use of hydroxy-compounds or hydroxyl solvents can be important since primary alcohols form hydrogen bonds when reacting with water, and the resulting properties of the compounds tend to be relatively water-miscible (NRC, 1989). Hydrocarbon solvents are selected based on their low aromaticity and role in enhancing the mixture of surfactants with oils of higher viscosity (USEPA, 1993). A well known example of a hydrocarbon solvent used in the chemical formulation of dispersants is the low-aromatic kerosene (NRC, 1989). Hydrocarbon solvents that have a branched chemical structure tend to be saturated with high boiling points and lower toxicity (USEPA, 1993).

2.3.1.2 Additives

Additives are present in the composition of chemical dispersants for two reasons that influence the efficacy of oil spill response as well as the dispersants themselves. One reason is because they can promote the dissolution of surface-active agents into the oil slick (NRC, 2005). A second reason is that certain additives can increase the longevity and stability of dispersant formulas so that they can be stored for longer periods of time while maintaining their chemical properties and be used during the ideal timeframe of an oil spill response (NRC, 2005).

2.3.1.3 Surfactants

Surfactants or surface-active agents are credibly the most essential compound existing in the makeup of chemical dispersants. These compounds are grouped into two categories that are
based on their balance of hydrophilic and lipophilic molecules, known as the hydrophile-lipophile balance (HLB), and type of ionic charge (Griffin, 1954; NRC, 2005). The scale for the HLB is measured from most lipophilic to most hydrophilic, and ranges from 1 to 20 (Griffin, 1954). According to Bancroft’s Rule (1913), a surfactant with a HLB range of 3 to 6 is primarily lipophilic, and would stabilize a water-in-oil emulsion, and a surfactant with an HLB range of 8 to 18 is primarily hydrophilic, and would stabilize an oil-in-water emulsion (NRC, 1989). For the purpose of dispersing oil in water, it is more effective to use surfactants with the HLB range of 8 to 18 (NRC, 2005). This relationship is defined as amphipathic, or having opposing solubility affinities, and explains why surfactant molecules reside at the oil-water interface, reduce oil-water interfacial tension by favoring hydrophilic molecules, and facilitate the formation of small oil droplets that disperse into the water column (NRC, 2005).

Surfactants are also categorized by charge type, generally anionic or negatively charged, cationic or positively charged, and nonionic or no charge (NRC, 2005). Cationic surfactants are not ideal to include in dispersant formulations currently used because they contain quaternary ammonium salts, which have a high toxicity to marine organisms (NRC, 2005). Most modern commercially available chemical dispersants consist of formulations with mixtures of nonionic (15 – 75 percent) and anionic (5 – 25 percent) surfactants, as well as those with higher and lower HLB so that the HLB values range from 9 – 11 (Wrenn et al., 2009). Corexit 9500A was primarily used for subsurface application during the DWH spill and contains a HLB value between 10 and 11, a formulation that facilitates better penetration into spilled oil and arguably higher efficacy for dispersing oil in marine environments (Tansel et al., 2014).

2.3.2 General Toxicity of Dispersants

The acute toxicity of first generation chemical dispersants became evident almost immediately after their use on the Torrey Canyon spill, with widespread mortality of marine organisms occurring in the water and on the shoreline (USEPA, 1993). While there was hesitancy to use chemical dispersants in the years after this spill, future research of toxicological effects and development of newer dispersants slowly soothed some of the negative perceptions associated with their application. Health concerns pertaining to the general toxicity of chemicals used during the dispersal process still exist, and questions are raised about the synergistic toxicity of dispersants and crude oil (NRC, 1989). It is generally accepted that vulnerability to
toxicological effects of both chemical dispersants and dispersed oil varies by species and life-stage, and higher toxicity values are evident for more sensitive embryonic and larval stage organisms (NRC, 2005). With that said, one of the main controversial issues regarding dispersant use being discussed and experimentally tested is the increased bioavailability of oil constituents to marine organisms and the potential increase in toxicity that results from effective oil dispersal in water (NRC, 2005).

2.3.2.1 Toxicity Testing

A substantial portion of the knowledge regarding toxicological effects of dispersants and concentration thresholds for various species has been derived from toxicity testing in laboratory settings under static exposures of 48 – 96 hour durations (Wolfe et al., 1998). To this day, academic, industry, and government sponsored research achieves conflicting results that support or contradict the suggested toxicological effects of chemical dispersants, as well as dispersed oil on the marine environment. However, many laboratory and manipulated experiments that expect to simulate natural effects of dispersed oil on marine organisms tend to use higher concentrations of lipophilic and hydrophilic TPHs (USEPA, 1993). This method has an ability to skew results because natural dispersion, aging, and weathering of oil in water can potentially reduce its concentration and toxic mechanisms (Anderson et al., 1987). In general, laboratory experiments that aim to determine acute toxicity and set threshold levels for marine organisms select a single organism and expose samples of the chosen organism to various concentrations of chemical dispersants, crude oil, and dispersant: oil mixtures (NRC, 2005). From the selection of modern toxicological studies that examine chemical dispersants and dispersed oil, most of them now agree that there is a higher toxicity associated with chemically dispersed oil than physically dispersed oil (Fingas, 2014). There are several factors that influence test results under controlled laboratory conditions, as listed in Table 2 below.
Table 2. Various Controlling Factors that Can Influence Toxicity Test Results for Marine Organisms (NRC, 2005).

<table>
<thead>
<tr>
<th>Controlling Factors for Determining Toxicological Effects of Dispersants on Marine Organisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Selection of test species and associated life-stage</td>
</tr>
<tr>
<td>2) Oil condition (fresh vs. weathered)</td>
</tr>
<tr>
<td>3) Methodology for preparing test solutions and dispersant: oil mixtures</td>
</tr>
<tr>
<td>4) Conditions of organism exposure to test solutions</td>
</tr>
<tr>
<td>5) Selection of organism response parameters</td>
</tr>
</tbody>
</table>

2.3.3 Chemical Dispersant Data Requirements

In order for a chemical dispersant to be considered for placement on the USEPA’s NCP Product Schedule, the manufacturer of the dispersant must submit its technical specifications to the USEPA (40 C.F.R. §300.920). Throughout the past several decades as newer, less toxic chemical dispersants have been formulated, the NCP Product Schedule has adapted to add these newer dispersants and remove older products (USEPA, 2014b; 40 C.F.R. §300.905). A list of the technical data that must be included in the manufacturer’s request for approval is presented below in Table 3.
Table 3. List of Technical Data Requirements for Chemical Dispersant Approval to USEPA NCP Product Schedule (40 C.F.R. §300.915).

<table>
<thead>
<tr>
<th>Data Requirements For Chemical Dispersant Approval Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Name, brand, or trademark under which dispersant is sold</td>
</tr>
<tr>
<td>2) Name, address, and telephone number of the manufacturer, importer, or vendor</td>
</tr>
<tr>
<td>3) Name, address, and telephone number of primary distributors or sales outlets</td>
</tr>
<tr>
<td>4) Special handling and worker precautions for storage and field application</td>
</tr>
<tr>
<td>5) Shelf life</td>
</tr>
<tr>
<td>6) Recommended application procedures, concentrations, and conditions for use depending upon water salinity, water temperature, types and ages of the pollutants, and any other application restrictions</td>
</tr>
<tr>
<td>7) Effectiveness (using Swirling Flask effectiveness test methods)</td>
</tr>
<tr>
<td>8) Dispersant toxicity</td>
</tr>
<tr>
<td>9) Reference standards from the American Society for Testing and Materials</td>
</tr>
<tr>
<td>i. Flash point</td>
</tr>
<tr>
<td>ii. Pour point</td>
</tr>
<tr>
<td>iii. Viscosity</td>
</tr>
<tr>
<td>iv. Specific gravity</td>
</tr>
<tr>
<td>v. pH</td>
</tr>
<tr>
<td>10) Dispersing Agent Components</td>
</tr>
<tr>
<td>11) Heavy Metals, Cyanide, and Chlorinated Hydrocarbons</td>
</tr>
<tr>
<td>i. Arsenic, cadmium, chromium, copper, lead, mercury, nickel, zinc, plus any other metals that may be reasonably expected to be in the sample</td>
</tr>
<tr>
<td>ii. Cyanide</td>
</tr>
<tr>
<td>iii. Chlorinated hydrocarbons</td>
</tr>
<tr>
<td>12) The technical product data submission shall include the identity of the laboratory that performed the required tests, the qualifications of the laboratory staff, including professional biographical information for individuals responsible for any tests, and laboratory experience with similar tests</td>
</tr>
</tbody>
</table>
2.4 Authorization Agreements

As previously stated under OPA90, the NRS is the tactical system in which the federal government responds to hazardous chemical and oil spills into all navigable U.S. waterways (NRC, 2005). The NRS is divided into three organizational levels that manage and coordinate emergency response among local, state, and federal agencies, as well as any responsible parties involved with the spill (NRC, 2005). These levels consist of the National Response Team (NRT), Regional Response Teams (RRTs), and Area Committees (NRC, 2005). The Federal On-Scene Coordinators (FOSC) charged with overseeing the timely, safe, and operational response to oil spills in marine environments, Great Lakes, and major navigable waters is the USCG (NRC, 2005). The USCG, along with the USEPA, function as co-chairs for NRTs and RRTs, with RRTs possessing authority over the application of chemical dispersants during an emergency response (NRC, 2005). The FOSC can authorize the use of chemical dispersants with the consent of representatives from the USEPA and RRTs, and with consultation from the U.S. Department of the Interior (DOI), U.S. Department of Commerce (DOC), and any federal natural resource agency that has jurisdiction within the impacted areas (NRC, 2005). Since the efficacy of chemical dispersants breaking down oil in water is significantly dependent on the time in which the oil is discharged and dispersants are applied, the NRT configured the NCP to implement authorization agreements that include three variations (NRC, 2005). According to USCG (2009) these agreements are defined as case-by-case approval, expedited approval, and pre-authorization, which are outlined in the U.S. as shown in Figure 3 below.
2.4.1 Case-by-Case Approval

The case-by-case approval agreement otherwise known as incident-specific RRT approval, mandates that the FOSC seek the approval of the RRT whose jurisdiction the impact area is located in (NRC, 2005). Other agencies that consider the decision to use chemical
dispersants in any given case are the USCG and USEPA (co-chairs), DOI, DOC, and state governments in which the spill has occurred (NRC, 2005).

2.4.2 Expedited Approval

As opposed to obtaining approval from the RRT, during an expedited approval agreement or quick approval, the FOSC can instead seek approval from several agencies which include the USCG and USEPA (co-chairs), and any applicable state or federal natural resource trustee agencies (NRC, 2005). A significant aspect of an expedited approval is the limited quantity and type of information that the FOSC is required to report to considering agencies, as well as the time that those agencies can take to either approve or disapprove the use of chemical dispersants (NRC, 2005). Situations where a quick approval may be necessary to disperse spilled oil are those that are time sensitive and occur near shorelines or in shallow waters. If all agencies required to grant an expedited approval request do not, the FOSC must then apply to the RRT to be considered as a case-by-case decision (NRC, 2005).

2.4.3 Pre-authorization

The application of chemical dispersants under a pre-authorization agreement relies on the sole discretion of the FOSC and does not require additional approval from any state or federal agency (NRC, 2005). Pre-authorization agreements are also known as pre-spill approvals, pre-approvals, or pre-spill authorizations, and are typically constrained by certain geographic locations, proximity to shorelines, season of year, and depth of water (NRC, 2005). In order to develop such preauthorization agreements, RRT representatives from the USCG, USEPA, DOC, DOI, and applicable state governments conduct net environmental benefit analyses (NEBA) to assess potential implications, positive or negative, associated with the application of chemical dispersants in that region (NRT, 2002). If executed in a timely manner, a pre-authorization agreement can potentially lead to effectively dispersing spilled oil in marine environments, based on the evaluations made by participating agencies (NRT, 2002).

2.5 Dispersant Application Methods

Depending on the geographic region, preapproval agreement, or extent of the oil spill, the chemical dispersants can be applied in several ways. The first method came about after the
Torrey Canyon tanker spill and involved a dispersant spraying system that was discharged from marine vessels (NRC, 2005). The ideology behind this method was to make the spraying process more manageable, and because dispersants during that time were undiluted hydrocarbon-based chemicals, they required anthropogenic agitation or mixing energy to facilitate dispersion (NRC, 1989). The development of third and fourth generation dispersant concentrates eliminated the need for anthropogenic agitation and its external equipment, limited the relative amount of chemical dispersants needed to break down the quantity of oil spilled, reduced the application rate, and prolonged the spraying time for a marine vessel or aircraft (NRC, 1989). In order to facilitate the formation of oil droplets with the multifaceted constraints that exist during dispersant application, it is crucial that the dispersants meet the following requirements outlined in Table 4.

Table 4. Seven Requirements for Chemical Dispersants to Facilitate Formation of Oil Droplets (NRC, 1989).

<table>
<thead>
<tr>
<th>Requirements for Chemical Dispersants to Facilitate Formation of Oil Droplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) The dispersant must be applied to the target oil slick or plume at the required dosage.</td>
</tr>
<tr>
<td>2) The surfactant molecules in the dispersant’s formula must have adequate time to penetrate the slick and mix evenly into the oil.</td>
</tr>
<tr>
<td>3) The surfactant molecules must orient at the oil-water interface with the hydrophilic groups in the water phase and the lipophilic groups in the oil phase.</td>
</tr>
<tr>
<td>4) The oil-water interfacial tension must decrease as a result of the presence of the surfactant molecules at the oil-water interface, thus weakening the cohesive strength of the oil film.</td>
</tr>
<tr>
<td>5) Sufficient mixing energy must exist or be applied at the oil-water interface to allow generation of smaller oil droplets.</td>
</tr>
<tr>
<td>6) The droplets must be dispersed throughout the water column by a combination of diffusive and advective processes to minimize droplet-droplet collisions and coalescence to form larger droplets.</td>
</tr>
<tr>
<td>7) After entrainment, the droplets must be diluted to nontoxic concentrations and remain suspended in the water column long enough for the majority of the oil to be biodegraded.</td>
</tr>
</tbody>
</table>
2.5.1 Marine Vessel Application

Prior to the widespread use of aerial application methods in the mid-1980s, marine vessels were the most common method of applying chemical dispersants to oil spills (USEPA, 1993). The outdated practice of deploying breaker boards behind marine vessels to externally agitate first and second generation dispersants became obsolete with the development of new chemical dispersant application systems that use water compatible concentrates able to be diluted with seawater (USEPA, 1993). The four components of standard equipment used on marine vessels are fitted to each individual vessel and consist of dispersant storage tanks, delivery pumps, a volumetric metering device, and the delivery system (USEPA, 1993). A commonly used system for delivering dispersants operates on a boom mounting arrangement, which is equipped with multiple spray nozzles that require constant flow rate, pressure, and pattern (USEPA, 1993). The relationship between dispersant spray width and oil that can effectively be dispersed is shown below in Table 5 (NRC, 1989).

Table 5. Dispersant Spray Capabilities of Marine Vessels Based on Spray Width and Chemical Volume Dispersed (NRC, 1989).

<table>
<thead>
<tr>
<th>System</th>
<th>Spray Width</th>
<th>Amount Disperseda</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Meters</td>
<td>Feet</td>
</tr>
<tr>
<td>One boat</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>One boat</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>One boat</td>
<td>80</td>
<td>100</td>
</tr>
</tbody>
</table>

a Calculation based on boat traveling at 6 kn, an average slick thickness of 0.1 mm, and 100 percent efficiency.

A tactical advantage to using marine crafts for applying chemical dispersants during an oil spill is the accessibility to the fleet that is equipped with dispersant delivery systems (NRC, 2005). This accessibility refers to the emergency response resources in marine environments where most spills occur, which include the dispersants themselves, fleet of vessels that can be rigged with delivery equipment, and the experienced ship captains and crew that can operate them on short notice (USEPA, 1993). Another advantage to using marine vessels can be observed when responding to small-scale oil slicks and spills, where smaller crafts can apply
chemical dispersants with higher maneuverability and precision closer to sensitive shorelines where larger vessels cannot (USEPA, 1993).

A significant disadvantage to using marine vessels when applying chemical dispersants is the relative magnitude of impacted area that an aerial craft can cover during large-scale spills (NRC, 2005). This disadvantage is attributed mainly to the slower speed that ships travel both from the nearest port to the spill site and through the oil slick itself (NRC, 2005). In addition, the obstructed ability of the ship’s captain and crew to visualize the overall scale of the spill and the effectiveness of dispersant application would require aerial instruction for directional feedback of their operation (USEPA, 1993). In regards to equipment function, if an oil spill occurs in arctic or sub-arctic marine environments then the efficacy of spray nozzles can be restricted due to aqueous-based solvent systems freezing at ambient temperatures below 0°C (NRC, 2005).

2.5.2 Aerial Application

The first fixed-wing aircraft and helicopter spraying systems used for applying chemical dispersants during oil spills developed in the 1970s and were innovated from agricultural systems (NRC, 1989). Airplanes can be retrofitted with chemical holding tanks, pumps that can spray twenty to one hundred liters per hectare (L/ha) or two to ten gallons per acre (gal/acre), digital readout flow meters, spray-booms, nozzles, and Geographic Information System (GIS) and Global Positioning System (GPS) technologies (NRC, 1989; USAF, 2013). Planes are typically the preferred method of surface dispersant application due to their ability to oversee a large impact area from the cockpit, travel for longer distances, and treat larger impact areas in shorter amounts of time (USEPA, 1993). Furthermore, their efficacy can be quantified by dispersant application volume per unit time. The dispersant carrying capacity of an aircraft and the high speeds in which they can travel is desirable for time sensitive spill response on which dispersant efficacy depends. Helicopters can match several advantages of the airplane for deploying dispersants during spill response with their higher maneuverability and storage convenience, even though they have a shorter range and carrying capacity than planes (NRC, 1989). Since the droplet size of the chemical dispersants influences their effectiveness, their discharge from an aircraft depends on the speed it is traveling, altitude it is flying, and wind speed that can cause fluctuations in application parameters (NRC, 1989).
Several disadvantages of aerial dispersant application are not directly related to the aircrafts themselves, but should be considered as shortcomings related to operational logistics. Spatial and legal barriers can negate the speed factor of using aircraft. Insurance and contractual agreements between involved industries must be negotiated such that they maintain access to dispersant-spraying aircraft that are relatively close to oil operations (NRC, 2005). Dispersant spraying equipment also requires routine maintenance and inspections to ensure that they will be functioning properly if they are ever required during emergency response. In addition, there are not enough readily-available aircraft that are equipped with dispersant spraying equipment or pilots and flight crews to operate them in a manner that the aerial application meets unique individual requirements of the spill response (USEPA, 1993). Two important requirements are the pilots’ ability to fly low altitudes at high speeds and ensuring that the dispersants are directly applied to the oil slick (USEPA, 1993). The altitude and speed requirements vary and are dependent on the size of both aircraft and the oil spill, as illustrated below in Table 6 (NRC, 1989).

Table 6. Dispersant Spray Capabilities of Aircrafts Based on Size and Chemical Volume Dispersed (NRC, 1989).

<table>
<thead>
<tr>
<th>Aircraft</th>
<th>Tank Volume</th>
<th>Amount Dispersed per Flight&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Meters&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Barrels</td>
</tr>
<tr>
<td>Various helicopters</td>
<td>0.4–2.3</td>
<td>2.5–15</td>
</tr>
<tr>
<td>Agriculture spray planes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piper Pawnee, Cessna, Agrtruck, and Ayres Thrush</td>
<td>0.4–1.1</td>
<td>2.5–7.3</td>
</tr>
<tr>
<td>Turbo Thrush</td>
<td>1.5–2.6</td>
<td>9.5–16</td>
</tr>
<tr>
<td>DC-3, Fokker F-27, and Canadair CL-215</td>
<td>3.0–4.5</td>
<td>19–28</td>
</tr>
<tr>
<td>Four-engine aircraft (DC-4, DC-6)</td>
<td>5.7–11</td>
<td>36–72</td>
</tr>
<tr>
<td>Hercules C-130, ADDS System</td>
<td>21</td>
<td>13</td>
</tr>
</tbody>
</table>

<sup>a</sup> Assumes dispersant-oil ratio is 1:20 and 100 percent efficiency of dispersion.
2.5.2.1 Modular Aerial Spray System

In 1988 the United States Air Force (USAF) developed a Modular Aerial Spray System (MASS) for their fleet of C-130 Hercules type aircraft capable of carrying 7,600 liters or 2,000 gallons of dispersants, with an additional Airborne Dispersant Delivery System (ADDS-Pack) capable of carrying 21,000 liters or 5,500 gallons (USEPA, 1993; USAF, 2013). When using the MASS the Hercules aircraft utilizes a spotter aircraft that flies behind at a higher altitude, and whose function is to provide feedback on alignment with the oil slick, spray patterns, and any adjustments needed for wind drift (USEPA, 1993). A Memorandum of Agreement (MOA) was established between the USCG and USAF in 1995, unifying the two branches to use chemical dispersants in response to large-scale oil spills, or Spills of National Significance (SONS) (USAF, 2013).

The U.S. Department of Defense (DOD) designated the Air Force Reserve's 910th Airlift Wing located at Youngstown Air Reserve Station in Ohio to maintain their only full-time, fixed-wing fleet of MASS capable aircraft, including four specially-modified C-130 Hercules aircraft (USAF, 2013). This Aerial Spray Squadron periodically conducts missions wherever necessary to eradicate biting insects such as mosquitoes, biting midges and filth flies, manage vegetation growth on military bomb-testing sites, and apply chemical dispersants when responding to oil spills (Kochansky, 2014).

2.5.3 Subsurface Injection

Prior to the 2010 DWH MC252 well blowout there had not been any large-scale subsurface application of chemical dispersants into deepwater and therefore no substantial scientific research exists regarding its efficacy in dispersing oil (Kujawinski et al., 2011). The novel characteristics of the DWH catastrophe and volume of oil discharged from MC252 forced the NRT to take a non-traditional approach in an attempt to curb the ecological injuries that the continuous spill was inflicting. The decision was made to inject chemical dispersants directly at the wellhead without any concrete evidence supporting whether the tactic would effectively break down the oil into droplets that would disperse into the water column, or if it would have any adverse effects on marine organisms by introducing additional toxins into the deepwater (Peterson et al., 2012). The application of chemical dispersants to the subsurface deep water wellhead during DWH was performed by using a jet stream that injected dispersant into the oil
and gas discharge coming from MC252, with the intended effects to mix the dispersant evenly with the oil and gas flow into the water column (Kujawinski et al., 2011).

2.6 Marine Ecosystems

No matter what stage crude oil and associated petroleum distillates are in their life-cycle, marine ecosystems are continuously exposed to accidental leaks or discharges of oil. Even if they occur on a small-scale these spills can still potentially have adverse impacts on the various ecosystems to which they are discharged. According to the NRS, a decision can be made by the NRT and RRT to apply chemicals dispersants in U.S. marine ecosystems, coastal areas, Great Lakes, and major navigable waters (NRT, 1994). Chemical dispersants can react differently within these ecosystems and results typically depend on the physical and chemical properties of the waters in which they are applied to (NRC, 2005). Such properties must be considered by the RRTs when spills occur in fresh, brackish, marsh, intertidal, and marine waters of varying temperature and salinity (Prince et al., 2013). The ecosystems where chemical dispersants have been applied to surface and subsurface waters that this research focuses on are the U.S. Gulf and Alaskan Coasts, where substantial petroleum operations occur and the risk of oil spills to their waters are a common threat. Injuries to marine organisms and negative effects on the trophic structure are also major concerns during an oil spill, especially when abundant and wide-ranging phyto- and zooplankton are exposed to chemical stressors, and have limited mobility to escape them (Wolfe et al., 1998). If these lower-trophic level organisms are exposed to the various chemical stressors of an oil spill, they can greatly influence the transfer of petroleum hydrocarbons and other hydrophobic organic compounds via their consumption by higher trophic-level organisms, consequent decomposition, and ultimate uptake by detritavores (Wolfe et al., 1996).

2.7 Chapter Summary

Chemical dispersants are typically considered as a secondary response method to oil spills instead of a primary direct cleanup method, and the decision for their application can be controversial due to the circumstantial effectiveness or regulations governing their use. There are several methods in which they can be applied to surface and subsurface waters, and systems exist to monitor the progress and efficacy of dispersant application.
Mechanical recovery and removal of spilled oil in marine environments is preferred as the initial response method because of the absence of potentially toxic chemicals being introduced to waters of the impacted area. Preapproval agreements, however, can be tailored to address regions in which chemical dispersants could in fact be the best primary response to an oil spill, so that they can be applied during the immediate timeline in which they are most effective.

Overall effectiveness regarding the use of chemical dispersants is a controversial subject due to various conflicting toxicity tests for marine organisms and a general disagreement over the best mechanisms for quantitatively and qualitatively evaluating the environmental tradeoffs for dispersant application. There is an extremely complicated relationship that exists between dispersants and their application to marine waters, and several factors that contribute to this complexity are the grade of oil spilled, concentration of chemicals used to disperse the spill, location where the spill occurred, politics and/or governance affecting dispersant application, and various other environmental, atmospheric, and biological conditions. The following chapter further discusses the application of chemical dispersants at the water’s surface.
CHAPTER 3 – DISPERSANT SURFACE APPLICATION

Prior to the 2010 DWH MC252 well blowout and resulting oil spill disaster, chemical dispersants had traditionally been applied only at the water’s surface during oil spill incidents, including those that had discharged from pipelines below the surface in shallow waters or waters less than 20 m (Peterson et al., 2012). When an oil spill occurs at or near the water’s surface and the response decision is made to apply chemical dispersants, the priorities are to minimize adverse ecological impacts to marine species and sensitive shorelines by reducing the oil into smaller droplets that can disperse into the water column (Kinner and Ballestero, 2012). Environmental and political conditions have seldom been consistent during actual emergencies, and various factors contribute to the efficacy of the response. These factors are outlined individually in the sections below and additionally when discussed with the selected case studies reviewed for surface application of chemical dispersants.

3.1 Oil Characteristics

Hundreds of different types of oils exist that contain different physical properties, thousands of hydrocarbon compounds, and unique characteristics for dispersion (USEPA, 1993). Typically, authorization agreements of any given region define which types or brand of chemical dispersants are approved for application onto the water’s surface (NRC, 2005). Yet, the type of oil spilled into that marine environment must first be identified in order to determine whether or not the approved dispersant would be effective in dispersing that particular grade of oil (USEPA, 1993). The transportation of crude oil and associated petroleum products at all life-cycle stages occurs often in surface waters in the U.S., and depending on the characteristics of the spilled oil, some grades of oil may easily be dispersed using chemicals, while other grades may not (USEPA, 1993). Intuitively, it would make sense to match dispersant formulations with oil type for increased effectiveness (NRC, 1989).

3.1.1 API Gravity Scale

The API gravity scale shown below in Equation 1 uses an algorithm to classify crude oils based on an inverse relationship between density of the oil and API gravity (USEPA, 1993). This relationship states that as the density of oil decreases, API gravity increases (USEPA,
1993). Normally refined crude oils tend to have API gravities ranging from 5 – 50 on the scale, where oils with API gravities below 5 are considered non-dispersible, and higher API gravities are indicative of more dispersible oil, as shown below in Table 7 (USEPA, 2011).

Equation 1. API Gravity Scale (USEPA, 1993).

\[
\text{API gravity} = \frac{141.5}{\text{specific gravity (60/60°F)}} - 131.5
\]

where: Specific gravity (60/60°F) is the oil density at 60°F divided by the density of water at 60°F.

Table 7. Chemical Characteristics of Whole Crude Oils (USEPA, 2011).

<table>
<thead>
<tr>
<th>Crude Source</th>
<th>Paraffins % vol</th>
<th>Naphthenes % vol</th>
<th>Aromatics % vol</th>
<th>Sulfur % wt.</th>
<th>API gravity (°API)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Light Crudes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saudi Light</td>
<td>63</td>
<td>18</td>
<td>19</td>
<td>2.0</td>
<td>34</td>
</tr>
<tr>
<td>South Louisiana</td>
<td>79</td>
<td>45</td>
<td>19</td>
<td>0.0</td>
<td>35</td>
</tr>
<tr>
<td>Beryl</td>
<td>47</td>
<td>34</td>
<td>19</td>
<td>0.4</td>
<td>37</td>
</tr>
<tr>
<td>North Sea Brent</td>
<td>50</td>
<td>34</td>
<td>19</td>
<td>0.4</td>
<td>37</td>
</tr>
<tr>
<td>Lost Hills Light</td>
<td>50% Aliphatics</td>
<td>-</td>
<td>50</td>
<td>0.9</td>
<td>&gt;38</td>
</tr>
<tr>
<td><strong>Mid range Crudes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Venezuela Light</td>
<td>52</td>
<td>34</td>
<td>14</td>
<td>1.5</td>
<td>30</td>
</tr>
<tr>
<td>Kuwait</td>
<td>63</td>
<td>20</td>
<td>24</td>
<td>2.4</td>
<td>31</td>
</tr>
<tr>
<td>USA West Texas sour</td>
<td>46</td>
<td>32</td>
<td>22</td>
<td>1.9</td>
<td>32</td>
</tr>
<tr>
<td><strong>Heavy Crudes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prudhoe Bay</td>
<td>27</td>
<td>36</td>
<td>28</td>
<td>0.9</td>
<td>28</td>
</tr>
<tr>
<td>Saudi Heavy</td>
<td>60</td>
<td>20</td>
<td>15</td>
<td>2.1</td>
<td>28</td>
</tr>
<tr>
<td>Venezuela Heavy</td>
<td>35</td>
<td>53</td>
<td>12</td>
<td>2.3</td>
<td>24</td>
</tr>
<tr>
<td>Belridge Heavy</td>
<td>Aliphatics 37%</td>
<td>63</td>
<td>1.1</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>
3.1.2 Viscosity

Viscosity is defined as a measurement for a fluid’s resistance to flow, and is another important characteristic of oil and how it relates to dispersant effectiveness (Clayton et al., 1992). A generally inverse relationship also exists between viscosity and API gravity, where oil containing a higher API gravity typically has a lower viscosity (USEPA, 1993). Two types of viscosities for crude oil are calculated when considering its flow in marine waters. The dynamic or absolute viscosity is equal to the shear stress divided by the rate of shear, and is typically measured in millipascal seconds (mPa.s) or centipoise (cP) (Bobra and Callaghan, 1990). Kinematic viscosity is measured in centistokes (cSt), defined as the ratio of dynamic or absolute viscosity to density, and is calculated by dividing the dynamic viscosity by the fluid mass density (Bobra and Callaghan, 1990). The temperature and weathering of oil are important factors when determining viscosity (Bobra and Callaghan, 1990). Although it was presumed during the 1980s that oils or emulsions with dynamic viscosities higher than 2,000 cP could not be chemically dispersed, laboratory experiments from Fiocco et al. (1999) and Guyomarch et al. (1999) showed in a controlled environment that various IFOs and emulsions with viscosities of approximately 20,000 cP could be dispersed in some measure (NRC, 2005). Corexit 9500 was one of the hydrocarbon solvent based dispersants used in these studies (Fiocco et al., 1999; Guyomarch et al., 1999). In a separate laboratory experiment conducted by Fingas et al. (2003), oil dispersibility with Corexit 9500 was measured using the swirling-flask laboratory test. Of the fourteen parameters tested for evaluating the effects of various physical and chemical properties on oil dispersibility, viscosity was determined to be the most significant physical property for oil dispersion (Fingas et al., 2003).

3.1.3 Oil Composition

Although viscosity was found to the most important physical property related to oil dispersion using Corexit 9500, several characteristics of chemical composition including concentrations of n-dodecane, n-hexacosane, and naphthalenes had a stronger correlation with oil dispersibility in a laboratory setting (Fingas et al., 2003). The primary hydrocarbons associated with crude oil are saturates, aromatics, polars, and asphaltenes, and they contain some naturally occurring surface-active compounds which contribute to the formation of mousse at the water’s surface (NRC, 2005). Because surface-active compounds in the crude oil can react erratically
with the surface-active compounds of a chemical dispersant, the relationship between oil composition and oil dispersibility is not predictable without challenge (NRC, 2005).

### 3.1.4 Residence Time

One of the most important parameters related to the efficacy of using chemical dispersants during an oil spill is the time window in which they are applied. Typically, the ideal time window for a response that involves surface application of dispersants varies depending on atmospheric and oceanic conditions (Lessard and Demarco, 2000). From the initial discharge of oil this time period ranges from twenty-four to seventy-two hours under temperate conditions, and twelve to twenty-four hours under arctic conditions (NRC, 2005). Time is truly of the essence because the longer the period in which oil floats at the water’s surface, the more spreading and weathering occurs, which also increases its viscosity (NRC, 2005). After a time period of twelve to twenty-four hours, the increased viscosity values of the spilled oil must be evaluated and a decision made whether or not applying chemical dispersants would have any beneficial use (NRC, 2005).

### 3.2 Oceanic Conditions

In addition to the characteristics of oil spilled in the incident and type of chemical used to disperse it, there are several variables related to the state of marine waters where the spill occurred that can influence the efficacy of dispersant application to the water’s surface. How the dispersed oil droplets enter the water column, mixing energy of the ocean, salinity, and temperature of the water must all be considered when applying chemical dispersants. These factors can potentially alter the shape of an oil slick and its concentration, and will be discussed in the sections below.

### 3.2.1 Water Column

One of the primary objectives of applying chemical dispersants to surface water after an oil spill is to facilitate the breakdown and transfer of oil droplets into the water column at a size of < 20 µm (USEPA, 1993). The physical or chemical transportation of these smaller oil droplets into the water column requires energy and consequently increases the interfacial area between oil-water (USEPA, 1993). A certain minimum energy is required to facilitate the
dispersion of oil droplets into the water column, and an estimation of this minimum amount of energy is defined below in Equation 2 (Fingas and Ka’aihue, 2004a). Furthermore, if the dispersant is applied under ideal conditions then the breakdown of oil from a single droplet into smaller droplets can begin to take place in a matter of seconds, as shown below in Figure 4.

Equation 2. Estimate for Minimum Energy Required for Oil Droplet Dispersion into Water Column (Fingas and Ka’aihue, 2004a).

\[
WK = \gamma_{o/w} A_{o/w}
\]

<table>
<thead>
<tr>
<th>WK</th>
<th>Mixing Energy [measured in ergs or g-cm(^2)-s(^{-2}); 1 erg equals 10(^{-7}) joule (kg-m(^2)-s(^{-2}))]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma_{o/w})</td>
<td>Oil-water Interfacial Tension (measured in dynes-cm(^{-1}), where 1 dyne equals 1 g-cm-s(^{-2}); equivalent to ergs-cm(^{-2}))</td>
</tr>
<tr>
<td>(A_{o/w})</td>
<td>Oil-water Interfacial Area (measured in cm(^2))</td>
</tr>
</tbody>
</table>

Figure 4. Breakdown of Single Oil Droplet into Smaller Droplets from Starting Time Zero at Milliseconds (ms) to 48 ms (Gopalan and Katz, 2010).
If the decision is made by the RRT that the spilled oil will inflict less damage or injury when dispersed into offshore deep water as opposed to spreading at the water’s surface, then there are several reasons for the logic behind this method. One reason is to remove the visible slick from the water’s surface so as to reduce the potentially mortal risk for vulnerable marine birds and mammals becoming coated with oil (Kinner and Ballestero, 2012). Another reason for breaking down the oil into the water column is to prevent an above-water slick from reaching and damaging shorelines that contain potentially more sensitive intertidal habitats for breeding, as well as commercial or recreational fisheries (Kinner and Ballestero, 2012). Complications can occur with oil dispersal in shallow waters with high sediment loads near coastlines, since the dispersed oil can undergo sedimentation, which occurs when suspended oil particles become entrained and rest against a barrier (Tamis et al., 2012). Other processes include adsorption to particulate matter and bioaccumulation into the sea bed, which can potentially threaten benthic marine organisms with chronic toxic exposure (Tamis et al., 2012).

3.2.2 Potential Mixing Energy

The application of chemical dispersants to surface waters can function at its peak performance with the presence of mixing energy, which redistributes the oil droplets both horizontally across the water’s surface and vertically into the water column (Kinner and Ballestero, 2012). Modern day chemical dispersant application systems do not require anthropogenic mixing as they previously did due to the new chemical dispersant application systems that use water compatible concentrates, which are able to be diluted with seawater (USEPA, 1993). Therefore, instead of relying on the external mixing technique, responders must take into consideration oceanic conditions including inclement weather, tidal energy, water turbulence, and water depth; all which can transform the oil slick, its concentration, and the efficacy of chemical dispersants (Gopalan and Katz, 2010). These hydrodynamic mixing conditions at the water’s surface in the marine environment can arguably be the most influential factors in the dispersal and residence time of spilled oil. For instance, the ocean’s tides and currents that are in motion during the spill can dictate the direction that the oil slick will travel, while swelling wave energy converts into mechanical mixing energy that not only disperses oil naturally but also bolsters the efficacy of chemical dispersal (Carls et al., 2001). Due to the variety of sources for potential mixing energy at the water’s surface and mechanisms in which
oil droplets can generate to disperse into the water column, it is improbable that a single parameter can be attributed to the overall mixing energy that disperses the oil (NRC, 2005).

### 3.2.3 Salinity

As concentrations of salinity range throughout fresh water (< 0.5 parts per thousand (ppt)), brackish water (0.5 – 30 ppt), ocean water (35 ppt), and brine water levels (> 40 ppt), dispersant formulations tend to react differently with these concentrations and their general effectiveness fluctuates (Tansel et al., 2014). Salinity concentrations in estuaries and coastal zones oscillate according to tidal flow, ocean currents, and wind energy, all of which influence the mixture of freshwater with ocean water (Tansel et al., 2014). In addition, even though salinity concentrations in estuaries typically increase with increased distance from the fresh water source, concentrations at the head of the estuary can exceed that of ocean water if enough evaporation occurs (Tansel et al., 2014). Unless mixing energy is constant and powerful enough to mix the water column of an estuarine ecosystem, salinity concentrations generally increase as water depth increases (Tansel et al., 2014). In general, there is little energy produced from hydrodynamic mixing in marine waters with low salinity, and therefore the application of chemicals to disperse and degrade spilled oil would not function at peak performance (Chapman et al., 2007).

Current commercially available chemical dispersants that are approved for marine surface water application are hydrophile-lipophile balanced, with formulations engineered in such a way that they react most effectively with ionic levels of natural seawater (Tansel et al., 2014). HLB is considered to have an important role in determining the effect of salinity on dispersant performance because hydrophobic portions of the surfactant molecule have an affinity for salting out effects, or becoming more soluble in ocean water containing very high ionic strength (Tansel et al., 2014). One significant result of these salting out effects is observed in marine waters with higher salinity that tend to decrease the interfacial tension between oil-water and enhance the dispersal of oil droplets into the water column (Chandrasekar et al., 2006). As previously discussed in Chapter 2, chemical dispersants containing lower values on the HLB scale would tend to stabilize a water-in-oil emulsion, whereas those with higher HLB values would tend to stabilize an oil-in-water emulsion (Bancroft, 1913). In a controlled laboratory experiment, Chandrasekar et al. (2006) found that salinity concentrations had the most significant role in
evaluating the importance of oceanic and atmospheric mixing energy and temperature for dispersant effectiveness based on the 648 different dispersant: oil combinations used in their study.

3.2.4 Temperature

The temperature of ocean water where oil has been spilled plays an important role in the interaction between spilled oil and chemical dispersants (NRC, 2005). Weathering parameters associated with this interaction include evaporation and the formation of water-in-oil emulsions or mousse, which are both directly related to temperature at the water’s surface (Fingas and Ka’aìhue, 2004b). The evaporation of dispersed oil droplets is enhanced during times of increased exposure of ultraviolet radiation and higher temperatures to the surface spill (Fingas and Ka’aìhue, 2004b). In colder waters, oils with higher viscosities promote the formation of emulsions at a higher rate because they can cause a stable slick to be thicker than 0.1 millimeter (mm), which can produce mousse (Fingas and Ka’aìhue, 2004b).

3.3 Atmospheric Conditions

In contrast to the various oceanic conditions that can influence the efficacy and fate of chemical dispersants and dispersed oil in marine waters, atmospheric conditions must also be considered. These variables include wind speed, wind direction, precipitation, and exposure to solar radiation. They can act independently or with oceanic conditions, and are discussed in the sections below.

3.3.1 Wind

Several properties of wind must be taken into consideration by response teams when applying chemical dispersants and predicting their pathway. Wind energy translates to turbulent energy in the ocean by means of shearing the water’s surface or producing waves at the water’s surface (Gopalan and Katz, 2010). Depending on the combination of wind speed and direction, response teams would have to manipulate their strategy for dispersant application such that they conform to the state of current weather conditions. If wind speeds at the site of an oil spill are exceptionally high [12 to 14 meters per second (m/s)], they will cause waves to break and produce localized areas of intense mixing, which can promote droplet formation (Fingas and
Ka’aihue, 2004a). At the same time these winds can hasten the spreading of an oil slick, which will in turn require a more rapid response time to treat the slick, and require an enhancement of dispersant delivery precision so that the spray nozzles do not miss the target area (USEPA, 1993). Otherwise known as rapid advection, during high winds this process transfers the oil horizontally across the water’s surface (NRC, 2005). According to Fingas and Ka’aihue (2004a), the minimum energy that is required from wind speed to degrade an oil slick into small droplets is 5 m/s.

### 3.3.2 Precipitation

Precipitation that occurs over a marine environment results in an added accumulation of fresh water that can mix with higher salinity marine waters. As discussed in the previous section, salinity plays an important role in the overall effectiveness of chemical dispersants, and concentrations can fluctuate based on marine mixing conditions, water depth, and proximity to fresh water sources. Because dispersant formulations are engineered to react with the ionic states of water in which they are applied, any oscillations in salinity that occur after the fact, or during response operations, are typically not considered and can present challenges in overall effectiveness (Fingas and Ka’aihue, 2004a).

### 3.3.3 Ultraviolet Exposure

Prolonged exposure to solar radiation can accelerate the photo-oxidation process of spilled oil at the water’s surface as well as other weathering processes (Glover et al., 2014). Photo-chemical oxidation results from the exposure of oil to air and sunlight, and occurs relatively slowly (first few days after initial spill) on surface water with most oils (Brandvik and Daling, 1998). Although the effect of photo-chemical oxidation may be insignificant on oil dispersibility with lighter oils, that is not the case with more waxy, higher viscosity oils, where photolysis can form stable water-in-oil emulsions after only several hours of ultraviolet exposure (Brandvik and Daling, 1998). On the other hand, fog and low clouds can constrain the aforementioned processes as well as cause logistical challenges and inhibit operations for aerial chemical dispersant application if the spotter or spraying aircraft are unable to see the oil slick or target area due to poor visibility.
3.4 Case Studies

The case studies of oil spill incidents in coastal waters of the U.S. where chemical dispersants had been applied to surface waters were selected for this research based on several factors. These include the varying ecosystems in which they occurred, atmospheric and marine conditions, mechanisms in which the oil was discharged, grade of oil discharged, class of chemical dispersant applied, emergency response tactics, and general effectiveness for dispersing oil. The aforementioned parameters for each case study are outlined in Table 8 below, and include the only deep water subsurface application of chemical dispersants, which took place during the BP DWH MC252 wellhead discharge. Background information on each case study was highlighted earlier in Chapter 1, and the following sections will delve deeper into the unique characteristics of the spill, response tactics, and a brief timeline of events that had occurred.
Table 8. Parameters Related to Each Dispersed Oil Incident Examined Throughout this Research

<table>
<thead>
<tr>
<th>Spill Incident</th>
<th>Ecosystem Source of Spill</th>
<th>Grade of Oil</th>
<th>Volume of Oil Spilled</th>
<th>Class of Dispersant</th>
<th>Volume of Dispersant Applied</th>
<th>Application Method</th>
<th>Mixing Conditions</th>
<th>Oceanic Conditions</th>
<th>Atmospheric Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/V Exxon Valdez</td>
<td>Arctic, Alaskan Coast</td>
<td>Alaska North Slope crude oil, API gravity 29.8</td>
<td>250,000 barrels, 11,000,000 gal</td>
<td>Corexit 9527</td>
<td>5,500 gal, 20,800 L</td>
<td>Initial helicopter attempts failed, aerial application completed via C-130</td>
<td>Initially little to no mixing. Heavy storm produced mixing after dispersant-use window closed</td>
<td>Deep, cold water (~5° C, 41° F) with low salinity</td>
<td>Initially calm and clear, heavy storm with 74-129 km/hr or 40-70 knot winds occurred two days later, decreasing visibility</td>
</tr>
<tr>
<td>M/V Blue Master</td>
<td>Gulf Coast</td>
<td>IFO 380, specific gravity 0.988</td>
<td>100 barrels, 4,200 gal</td>
<td>Corexit 9500</td>
<td>700 gal, 2,660 L</td>
<td>Aerial application via C-130, with spotter aircraft</td>
<td>Low mixing, calm seas concentrated oil in a current-generated convergence zone</td>
<td>Calm seas, weak surface currents, and two currents collected oil along converged line</td>
<td>Clear, warm temperatures, light winds</td>
</tr>
<tr>
<td>Poseidon Pipeline</td>
<td>Gulf Coast</td>
<td>Sweet Louisiana crude oil, API gravity 31.5</td>
<td>2,000 barrels, 84,000 gal</td>
<td>Corexit 9527</td>
<td>6,000 gal, 22,700 L</td>
<td>Aerial application via DC3 and DC4 aircraft</td>
<td>4-6 foot seas ideal for oil dispersion</td>
<td>Water depth: 400 feet, 122 m. Slick transported by Gulf of Mexico Loop Current</td>
<td>18-28 km/hr or 10-15 knot winds</td>
</tr>
<tr>
<td>Spill Parameter</td>
<td>Ecosystem</td>
<td>Source of Spill</td>
<td>Grade of Oil</td>
<td>Volume of Oil Spilled</td>
<td>Class of Dispersant</td>
<td>Volume of Dispersant Applied</td>
<td>Application Method</td>
<td>Mixing Conditions</td>
<td>Oceanic Conditions</td>
</tr>
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<tr>
<td><strong>Spill Incident</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Eugene Island Pipeline</strong></td>
<td>Gulf Coast</td>
<td>Pipeline leak presumably due to aging infrastructure</td>
<td>Eugene Island crude oil, API gravity 33.7</td>
<td>1,500 barrels, 63,000 gal</td>
<td>Corexit 9527</td>
<td>1,100 gal, 4,160 L</td>
<td>Aerial application via five sorties over three day period, equipped with King Air spray platform</td>
<td>Initial 1-2 foot light seas, slight easterly coastal current drift, intensified during dispersant application to ~5 foot seas</td>
<td>Spill occurred at 18 m depth, light sea state prevented faster surface transport</td>
</tr>
<tr>
<td><strong>Deepwater Horizon MC252 (Surface Application)</strong></td>
<td>Gulf Coast</td>
<td>MC252 wellhead blowout</td>
<td>Macondo crude oil (ENT-052210-178), API gravity 35.6</td>
<td>4,900,000 barrels, 206,000,000 gal</td>
<td>Corexit 9500 and Corexit 9527</td>
<td>1,400,000 gal, 5,300,000 L</td>
<td>Aerial application via 12 C-130 aircraft, spraying over a period of 61/90 days</td>
<td>Mixing processes at the subsurface and weathering influenced oil that rose to surface slick</td>
<td>Discharge point of 1.5 km, horizontal deep water currents</td>
</tr>
<tr>
<td><strong>Deepwater Horizon MC252 (Subsurface Application)</strong></td>
<td>Gulf Coast</td>
<td>MC252 wellhead blowout</td>
<td>Macondo crude oil (ENT-052210-178), API gravity 35.6</td>
<td>4,900,000 barrels, 206,000,000 gal</td>
<td>Corexit 9500</td>
<td>770,000 gal, 2,900,000 L</td>
<td>Subsurface injection directly at MC252 using jet stream applied from marine vessel</td>
<td>Substantial quantities of natural gas caused oil buoyancy. Pressure of well explosion dispersed oil. Shifting ocean currents shifted surface oil expression</td>
<td>At 1,500 m depth: horizontal currents, high pressure, and temperature influence DSD and rate of vertical rising</td>
</tr>
</tbody>
</table>
3.4.1 T/V Exxon Valdez (1989)

The single-hull of the T/V Exxon-Valdez struck Bligh Reef in 1989 and discharged 250,000 barrels of Alaska North Slope crude oil just 1.8 km from the western shores of Bligh Island in Prince William Sound (Boufadel and Bobo, 2011). At the time, this incident was considered to be the largest oil disaster that had occurred in U.S. waters. Approximately 2,000 km of rocky, intertidal shorelines within the Gulf of Alaska were impacted by the spill, and a study by scientists from NOAA found that refractory subsurface oil from the spill is still present along the beaches of Prince William Sound in the amount between 60 – 100 tons (Short et al., 2004). From March 24th to June 20th, 1989, spilled oil from the T/V Exxon Valdez had been distributed throughout an area approximately 28,500 km² within the Gulf of Alaska, as observed below in Figure 5 (Piper and Munson, 1996).

Figure 5. Distribution of T/V Exxon Valdez Oil in the Gulf of Alaska from March 24th – June 20th, 1989 (Piper and Munson, 1996).
The properties of Alaska North Slope crude oil (API gravity = 29.8) are known to have relatively high concentrations of polycyclic aromatic hydrocarbons (PAHs) and asphaltenes, which characteristically form stable emulsions in the cold (< 5° C), low salinity Arctic waters (NRC, 2005). Since the spill occurred only 1.8 km from the shoreline and during a severe storm that aggravated the distribution of crude oil and chemically dispersed oil, there were immediate and observable impacts on wildlife throughout the entire region (NRC, 2005). In the span of the cleanup it was estimated that 2,800 sea otters, 300 harbor seals, and 250,000 birds were mortally wounded due to oil exposure (Piper and Munson, 1996). Aside from ecosystem impacts, the spill severely damaged commercial fishing industries in the Gulf of Alaska. It is estimated that approximately 11,000 people were deployed to respond to the Exxon Valdez spill, spending $2 billion throughout 1989 – 1992 (NRC, 2005).

The T/V Exxon Valdez struck Bligh Reef at the time of 0004 on March 24th, 1989, and sent out distress calls to local authorities (Piper and Munson, 1996). Approximately twelve hours after the collision occurred, response teams began arriving at the scene. Two skimmers were dispatched to mechanically recover the spilled oil from the water’s surface and transfer oil from the Valdez to the lightering tanker Exxon Baton Rouge (NRC, 2005). It was an ominously coincidental occurrence that the first pre-approval zones in the U.S. were approved by the Alaskan RRT just two weeks prior to the Exxon Valdez spill (NRC, 2005). The decision to apply chemical dispersants was already sanctioned in Zone 1, and was carried out even though weather conditions were relatively calm with little mixing energy during the first two days following the spill (NRC, 2005). The aircraft readily available to apply chemical dispersants were helicopters and C-130s; however, there was only one helicopter bucket spray system that was stored nearby and no large-scale application packages for the C-130 (ADDS-Pack) (NRC, 2005).

Within the first three days after the spill, there were four attempts to apply chemical dispersants using helicopter bucket spray systems. The first two applications of Corexit 9527 were completed via helicopter, with the first occurring twelve hours after the spill, and the second taking place on the morning of March 25th, 1989 (NRC, 2005). The third application attempt during the morning of the third day, March 26th, had failed due to a malfunction with the bucket spray applicator, and the fourth and final helicopter attempt was completed later that afternoon (NRC, 2005). A winter storm had begun to enter the Gulf of Alaska on March 26th,
and produced initial conditions of poor visibility to inhibit monitoring activities for the final helicopter application (Piper and Munson, 1996).  With the severity of the storm increasing, a C-130 equipped with an ADDS-Pack was deployed on the morning of March 27th, approximately 80 hours after the initial spill, and applied 20,800 L of Corexit 9527 around a 1 mi buffer zone of the T/V Exxon Valdez (NRC, 2005).  Unfortunately, the 40 – 70 knot winds produced powerful atmospheric and oceanic mixing conditions when dispersants were applied by the C-130 aircraft, and the T/V Exxon Valdez and Exxon Baton Rouge with their crews were sprayed with Corexit 9527 (NRC, 2005).  Due to this additional contamination and cleanup operation along with Exxon’s inability to effectively target and apply chemical dispersants, the State of Alaska rescinded the permission to use dispersants during that incident (Piper and Munson, 1996).  As a result of the painful lesson learned from sailing in dangerous waters with vulnerable single-hulled tankers, many nations have prohibited such tankers to be commercially sailed (Piper and Munson, 1996).  In addition, within two decades after the Exxon Valdez disaster, approximately 80% of super tankers worldwide were built with double-hulls, or a reinforcing buffer layer of steel that could reduce discharge in an accident (Piper and Munson, 1996).

3.4.2 M/V Blue Master (1999)

The M/V Blue Master inadvertently collided with the F/V Captain on August 27th, 1999, and resulted in a 1 ft² hole in the fuel tank of the M/V Blue Master (Kaser et al., 2001).  This leak continued for a period of 30 minutes, until the level of fuel in the ship’s tank equaled the point of impact at the tank, and discharged approximately 1,000 barrels of IFO 180 (specific gravity = 0.988) into Gulf of Mexico waters, located nearly 55 mi south of Galveston, Texas (NRC, 2005).  Even though several important conditions existed during this spill that did not meet the parameters required for dispersant pre-approval, the RRT permitted the application of chemical dispersants regardless (Kaser et al., 2001).  The oil varied in thickness and was concentrated in a wind and current convergence line shaped like a fish hook that spanned approximately 4 nautical miles (Kaser et al., 2001).  One of the only available pieces of monitoring and response data is a hand-sketch that was used by the Unified Command to diagram the spill, shown below in Figure 6.
As mentioned in the previous section, there were several important conditions that were beyond the limits of the pre-approval agreement established by the Region VI RRT for the application of chemical dispersants. For instance, the low mixing energy that was produced by calm seas and light winds raised concern that the Corexit 9500 would not mix uniformly with the oil (Kaser et al., 2001). The presence of converging offshore currents allowed the IFO 180 to remain concentrated in the same geographical region along a convergence line, whereas the lack of surface currents allowed the oil at the water’s surface to resist emulsification (Kaser et al., 2001). The lack of weathering and emulsification exhibited by the spilled IFO 180 contributed to the decision to allow the application of chemical dispersants outside of the six hour timeframe, which was the tail-end of the pre-approval window (Kaser et al., 2001). The reason for the lag of time was due to the Unified Command being unable to initially assess and verify the magnitude of the spill so that they could deploy aircraft with relative amounts of dispersant (Kaser et al.,
There were also slight socioeconomic pressures to respond quickly and effectively to this spill, which required applying dispersants within the pre-approval window, since the Labor Day holiday was two weeks away and nearby beaches functioned as popular tourism destinations (Kaser et al., 2001).

The specific gravity of IFO 180 (0.988) was outside the upper limit for the guidance range on dispersible oils (0.953), which are categorized as “probably difficult or impossible to disperse” (Kaser et al., 2001). That being said, the guidance documents and research for pre-approval agreements were conducted in the 1970 – 80s, and based upon the capabilities of previous generation dispersants such as Corexit 9527, which were likely unable to effectively disperse heavier, emulsified, or weathered oils (Kaser et al., 2001). The Scientific Support Coordinator (SSC) from NOAA predicted Corexit 9500 to have an effectiveness rate of 0 – 50% in dispersing IFO 180 due to the existence of unfamiliar circumstances (Kaser et al., 2001). It was determined that the upper effectiveness rating of 50% for Corexit 9500 would be greater than what could be accomplished via mechanical recovery or no response (Kaser et al., 2001).

Another irregularity with the conditions of the pre-approval agreement was the dispersant: oil ratio that was used for dispersing IFO 180. 2,660 L of Corexit 9500 were applied to the water’s surface, which accounts for a 1:6 dispersant: oil ratio (NRC, 2005). This ratio was much greater than the 1:20 target ratio as well as the 1:10 upper limit ratio defined by the NCP requirements at that time (Kaser et al., 2001). The RRT determined that since IFO 180 is a heavier, higher viscosity residual oil, it would not typically spread or disperse in the same manner as a lighter, less viscous oil (Kaser et al., 2001). The decision to apply Corexit 9500 in that amount was justified by their prediction that increasing the application value would increase the amount of dispersant that would come into contact with the oil (Kaser et al., 2001).

The evaluations from the Unified Command and the USCG regarding both efficacy and success were based on two observations. First off, visible reductions of IFO 180 were seen both at the water’s surface slick and when only 1.5 barrels of tar balls washed up along the shoreline two weeks later (Kaser et al., 2001). The second reason was due to there being no reports of marine organisms or birds that were adversely impacted or injured by the spilled oil (Kaser et al., 2001). Due to the aforementioned reasons, the Unified Command considered the response tactics used during this incident to be a “cautious success” (NRC, 2005). Nonetheless, since obtaining the terms of a pre-approval agreement was a stretch, the benefits of full-scale SMART
resources were not available during the response as they typically would be (NRC, 2005). Although Tier I monitoring was accomplished by USCG personnel who performed visual monitoring of dispersant effectiveness, Tier II monitoring was unavailable within the timeframe required and therefore could not provide a quantitative analysis of the efficacy of Corexit 9500 dispersion of IFO 180 into the water column (Kaser et al., 2001).

3.4.3 Poseidon Pipeline (2000)

The Poseidon Pipeline was struck by an 8.8 metric ton anchor on January 21st, 2000 and with its flukes attached, caused a 204 m displacement of the pipeline, dragged from its original location (Stoermer et al., 2001). This incident resulted in the discharge of 2,000 barrels of Sweet Louisiana crude oil into Gulf of Mexico waters approximately 105 km south of Houma, Louisiana, from three different locations along the pipeline (Stoermer et al., 2001). The discharge points of the pipeline were located at a depth of approximately 400 feet or 122 m, as well as at an offshore drilling platform one mile away, shown below in Figure 7 (Stoermer et al., 2001). The surface oil slick was predicted to reach shorelines within several days, and due to the high risk for environmental injury the use of chemical dispersants was authorized by the Region VI RRT under the newly revised pre-approval agreement (Stoermer et al., 2001). Unlike the M/V Blue Master spill reviewed earlier, SMART teams from the USCG GST were deployed for both Tier I/II monitoring operations during this Poseidon Pipeline incident.
The properties of S. Louisiana crude oil (API gravity = 31.5) discharged from the Poseidon Pipeline were slightly sour with medium viscosity, having tendencies to form refractory tarballs and be transported across the water’s surface for long distances (Stoermer et al., 2001). The oil slick did not behave as the preliminary trajectories had predicted them to. Instead of reacting to a Northwesterly movement, the slick’s movement was being influenced by a gyre off the Gulf of Mexico Loop Current and moved to the Southeast (Stoermer et al., 2001). Based on the fluctuations of the spill’s movement observed through trajectory modeling, the application of chemical dispersant Corexit 9527 commenced at 1530 on January 21st, and concluded on the 22nd (Stoermer et al., 2001). Over these two days, a total of 22,700 L of Corexit 9527 were applied via aircraft over the target area of the slick at the water’s surface.
The response tactics for this pipeline discharge incident were considered to be successful by the Unified Command, and several fundamental steps for chemical dispersant application and monitoring adhered to the SMART Protocols. From 1530 to dusk on January 21st, 11,350 L of Corexit 9527 was applied to the surface slick (3,780 L via DC-3 and 7,570 L via DC-4), and was visually monitored using SMART Tier I protocols, which predicted 75% of the surface oil had been dispersed (Stoermer et al., 2001). The following day after a preliminary overflight of the impact area showed patches of oil which could potentially be dispersed, the DC-3 effectiveness test was carried out and applied 3,780 L of Corexit 9527 to the target area at the water’s surface (Stoermer et al., 2001). Immediately following that test, reconnaissance aerial missions observed surface herding effects from the dispersant application, but could not locate a dispersant plume. The SMART team in marine vessels used data recorded from their on-water fluorometric measurements to associate Corexit 9527 application and dispersant effectiveness as part of SMART Tier II protocols. Based on the observed effectiveness of Corexit 9527, an additional 7,570 L was applied via DC-4 (Stoermer et al., 2001). During the last overflight by SMART aircraft personnel, the only visible oil left at the water’s surface were scattered patched of emulsified oil, which was determined to be not dispersible (NRC, 2005).

The successful implementation of Tier I/II SMART monitoring facilitated the effective application of Corexit 9527 during this Poseidon Pipeline incident without any recorded injury to wildlife (Stoermer et al., 2001). The Poseidon Pipeline has the capacity to transport roughly 500,000 BPD, and the alarm set off by abnormal pressure variations caused by the leak prompted operators to shut down the pipeline, which is the reason why only 2,000 barrels were discharged (Stoermer et al., 2001). There were important lessons learned during the M/V Blue Master incident and others in the Gulf of Mexico regarding deficiencies within the pre-approval process. On January 19th, 2000, the RRT had approved several key changes to the pre-approval agreement process that provided the FOSC more flexibility for adaptation throughout an oil spill incident (Stoermer et al., 2001).

3.4.4 Eugene Island Pipeline (2009)

On July 25th, 2009, an alarm indicated a drop in pressure along the Eugene Island Pipeline System in Louisiana, but there was no known location of any leak (Fletcher, 2014). The following day, the USCG Marine Safety Unit (MSU) Morgan City had reported an oil spill
located 48 km offshore the Louisiana Coastline and 97 km southwest of Houma, Louisiana, which was estimated to have an initial discharge of 1,500 barrels of Eugene Island crude oil (Fletcher, 2014). The cause of this leak in the 173,000 BPD capacity Eugene Island Pipeline System had been speculated to be a direct result of aging infrastructure, staining, and corrosion of the pipeline system (Fletcher, 2014). The location of discharge along the 20 inch pipeline was at a water depth of 18 m, and resulted in a visible oil slick that spanned over a 207 km² area in the Gulf of Mexico (Oil Spill Intelligence Report, 2009). After the slick was observed on July 26th, MSU Morgan City had made a request for USCG GST backing for dispersant application and monitoring activities (Fletcher, 2014). The following morning, Shell Pipeline had made a request to apply chemical dispersants to the slick at the water’s surface, and were authorized under the Region VI RRT pre-approval agreement (Fletcher, 2014). Lapses in communication between the GST SMART teams, Marine Spill Response Corp, and the NOAA SSC at the ICP in New Orleans, Louisiana resulted in the utilization of only Tier I monitoring, even though Tier II/III teams were available (Fletcher, 2014).

Even though not much data exists on the properties of the Eugene Island crude oil (API gravity = 33.7), it is classified as a light crude deemed to be dispersible by Corexit 9527 under the mixing conditions present during the incident (Fletcher, 2014). The initial trajectory analysis provided by the NOAA ERD predicted light to variable winds and on-shore transport conditions for the oil slick and landfall to occur within several days (Fletcher, 2014). With that determined, weather conditions had fluctuated throughout the incident response and the trajectory of the oil slick became increasingly difficult to predict, which contributed to the lapses in communication for monitoring activities (Fletcher, 2014). In order to reduce overall environmental impact, dispersant application missions commenced on July 27th, 2009, and concluded on July 30th (Fletcher, 2014). Over these two days, a total of five sortie missions were deployed which applied approximately 4,160 L of Corexit 9527 to the target areas of the oil slick (Fletcher, 2014).

Overall, the FOSC and NOAA SSC were satisfied with the level of effectiveness Corexit 9527 had in dispersing the oil slick produced by the Eugene Island Pipeline spill, even though the information regarding SMART operations was sparse and application teams from Marine Spill Response Corp. were unable to coordinate with Tier II/III teams (Fletcher, 2014). On July 27th, a SMART Tier I team provided visual observations without the presence of Tier II/III teams
for the first sortie mission. Later that day, Tier II/III teams with monitoring equipment were present in the general area of incident response, but the fluctuating weather was blamed for the last minute change in target area of the slick that caused them to be absent yet again (Fletcher, 2014). Both sortie missions were equipped with King Air spray platforms and applied 1,890 L of Corexit 9527 to the oil slick (Fletcher, 2014). Tier I monitoring was available for a third dispersant application sortie deployed on July 28th, but there is some degree of confusion between the Fletcher Report (2014) and the NOAA ERD whether chemical dispersants were actually applied that day. The final two sortie missions occurred on July 29th, the third day of dispersant activities, applying 2,270 L of Corexit 9527 (Fletcher, 2014). Although there was no Tier II/III support for these application sorties, the reporting conducted by Tier I teams indicated that the dispersants were effective, as shown below in Figure 8.

Figure 8. Flight Path of Sortie Mission #4 on July 29th, 2009 for Eugene Island Pipeline Response (Fletcher, 2014).
The Eugene Island Pipeline spill is a classic example of how communication breakdown can occur within ICS. The lack of support from Tier II/III SMART equipment and personnel is evident in the monitoring and reporting processes. With that said, even though the FOSC urged for the utilization of Tier II/III teams, the NOAA SSC determined that Tier I monitoring data was sufficient for the response effectiveness, and doubted that Tier II/III data would have altered recommendations made to the FOSC in any way (Fletcher, 2014). Indeed, the application of chemical dispersant Corexit 9527 may have facilitated the breakdown of the surface slick, but several key failures could have presented much larger problems in a different scenario. The lack of communication between various levels of the response structure, the lack of a standard procedure requirement of written logs, and the lack of utilization of Tier II/III equipment, technology, and personnel were apparently not vital issues with this incident, although they should serve as lessons learned for future incidents.

3.4.5 Deepwater Horizon (2010)

At 2300 on April 20\textsuperscript{th}, 2010, one of the worst oil spill catastrophes on record occurred when the MC252 wellhead, located 1.5 km below the water’s surface, experienced a blowout that caused a fire and explosion on the rig of Deepwater Horizon (DWH), causing it to sink into waters approximately 90 km offshore the Louisiana Coast in the Mississippi Canyon in the Gulf of Mexico (Kujawinski et al., 2012). The explosion itself caused the death of 11 rig workers and injured 17 more (NRC, 2013). The rate, magnitude, and depth at which the Macondo crude oil [(ENT-052210-178) (API gravity = 37.2)] was being discharged from MC252 caused the incident response strategies to be extremely complex and challenging, and prompted the declaration for a SONS (Tamis et al., 2012). Depending on the variations in pressure, the volume of Macondo crude oil discharged at MC252 was flowing at rate between 50,000 – 70,000 BPD (Spier et al., 2013). Although some sources have calculated slightly different numerical figures for the total amount of crude oil discharged, the generally accepted figure is 206,000,000 gallons or 4,900,000 barrels (Spier et al., 2013). This section focuses on the dispersant application during DWH at the water’s surface, whereas Chapter 4 focuses on dispersant application at the subsurface.

Chemical dispersant application was authorized under the Region VI RRT pre-approval agreement and SMART Protocol monitoring was initially conducted by the USCG National
Strike Force (NSF), before additional assistance came from industrial contactors and other divisions of the USCG (Fletcher, 2014). SMART monitoring results were reported by the USCG and NOAA SSC to the FOSC at the ICP in Houma, Louisiana (Fletcher, 2014). Aerial dispersant application commenced on April 22\textsuperscript{nd}, 2010, and concluded on July 19\textsuperscript{th} of that year, marking the longest period of chemical dispersant application in U.S. history (Fletcher, 2014). Of this 90 day dispersant application period, 61 of these days involved active spraying that utilized 412 sortie missions and 5,300,000 L of Corexit 9500 and Corexit 9527 at the surface oil slick over an area spanning 46,000 km\textsuperscript{2} (Fletcher, 2014). There were 118 SMART Protocol missions associated with DWH, the breakdown being 77 Tier I, 30 Tier II/III, and 11 Tier III+, until MC252 was capped on July 15\textsuperscript{th}, 2010 (Fletcher, 2014).

Unique characteristics and complications that arose from this incident expanded throughout the entire incident response process. Predicting the transport of the surging oil from MC252 at a depth of 1.5 km to the water’s surface proved to be extremely difficult, and unforeseen factors regarding pressure and natural oil dispersion had tremendous effects on the efficacy of dispersant application to the crude oil that had reached the water’s surface (Spier et al., 2013). Macondo crude oil that had reached the surface in the incredible high volume that it did could not be contained or collected by the available mechanical recovery equipment (Fletcher, 2014). From April 28\textsuperscript{th} to July 19\textsuperscript{th}, 2010, the Offshore Operations Branch of the ICP conducted 411 ISBs, removing roughly 5\% of the total amount of discharged oil (Fletcher, 2014). The surface oil spread rapidly to an eventual area of approximately 75,000 km\textsuperscript{2} in the Gulf of Mexico, which consisted of open ocean, sensitive wetlands, marshes, intertidal areas, and beaches, with the spatial extent of the spill relative to its source shown below in Figure 9 (NRC, 2013).
Figure 9. Spatial Extent of 2010 DWH Oil Transport in Gulf of Mexico (NRC, 2013).

The 2010 DWH incident was the first implementation of SMART capabilities during a SONS (Fletcher, 2014). Since the only full-time, fixed-wing, large-area aerial spray unit operated by the DOD during the DWH SONS was the Air Force Reserve’s 910th Airlift Wing in Youngstown, Ohio, they were recruited to assist in dispersant application activities, in accordance with the 1996 MOA between the USAF and USCG (USAF, 2013). SMART Tier I/II/III monitoring conducted standardized observation and measurement operations during the course of surface dispersant application. The Tier I monitoring consisted of aerial reconnaissance of dispersant effectiveness that reported results using high-resolution photography equipment and standardized documentation forms (Fletcher, 2014). An added
benefit of having SMART Tier I operating out of ICP Houma was the ability of response teams
to hand deliver their observation results to command staff. The option to digitally upload
observations from the field to an EPA online database was made available to increase ease of
access (Fletcher, 2014).

Tier II/III monitoring utilized most of the same equipment and reporting protocols,
although Tier II required fluorometry testing at a 1 m depth of the water’s surface, while Tier III
required fluorometry testing at multiple depths up to 10 m, both before and after chemical
dispersant application (Fletcher, 2014). When taking fluorometric measurements, Tier III teams
positioned portable water labs, Hydrolab DataSonde, that could record additional properties of
the water, including pH, temperature, conductivity, dissolved oxygen, and turbidity (Fletcher,
2014). The revolutionary addition to the SMART Protocols was Tier III+ monitoring, which
operated a Laser In-Situ Scattering and Transmissometry (LISST) multi-parameter instrument,
which was capable of calculating particle size distribution under various states of weathering and
sea states (Fletcher, 2014). Tier III+ monitoring teams were used mostly in conducting
dispersant efficacy tests during subsurface application, which is discussed in Chapter 4.

3.5 Chapter Summary

There is a wide variety of conditions that can affect or alter a chemical’s ability to
disperse oil at the ocean water’s surface into the water column. More often than not, these
conditions are dependent on each other. The physical and chemical composition of an oil, along
with the water state in which it is discharged, are factors in which can determine what class of
chemical dispersant to apply. Other factors deriving from oceanic and atmospheric conditions,
most importantly potential mixing energy, salinity, and temperature, can also influence a
chemical’s dispersibility of oil at the water’s surface. The case studies presented are
representative of the variety of different spill conditions and response methods that took place in
marine waters of the U.S. Chapter 4 focuses on environmental dynamics relating to chemical
dispersants applied to deep water during subsurface discharges, chiefly the 2010 BP DWH
MC252 well blowout.
Although chemical dispersants had been a resource available to combat against oil spill incidents for decades, including those that had occurred below the water’s surface, they had not been deliberately applied to deep water subsurface spills until the BP DWH MC252 well blowout in 2010. During the hectic response operations, legal counsel for BP emphasized that surface application of chemical dispersants was the only contemplated application method considered during the most recent revision of the NCP at the time in the 1990s (Iaquinto, 2012). Due to the extremity of the continuous leaking of oil from MC252 from a depth of 1,500 m during the DWH disaster, the unprecedented method of subsurface application of chemicals was used to attempt to disperse this oil without any concrete understanding of potential backlash or recourse. In the following sections of this chapter that describe conditions related to dispersant subsurface application, the DWH case study will be referred to often since it is the only incident in which chemical dispersants were applied at such a depth and many subsequent studies tend to simulate its conditions in order to influence future management strategies.

4.1 Oil Characteristics

This chapter focuses on the application of chemicals to disperse oils discharged below the water’s surface, and the types of oil that can be treated with chemicals are limited by several factors. The spilled oil would have to originate from submerged releasing ports, such as deepwater extraction wells or pipelines, at depths where the oil would initially remain in the water column as a plume instead of emerging up to the water’s surface to form a slick (Zhao et al., 2014). In the case of the 2010 DWH MC252 wellhead blowout, the type of oil being discharged was Macondo crude oil (ENT-052210-178), with an API gravity of 37.2, at a depth of approximately 1,500 m (Tamis et al., 2012). This particular type of oil is a light crude with a density in water of 0.839 grams per cubic centimeters (g/cm$^3$) at 15° C, and 0.825 g/cm$^3$ at 35° C (Lehr et al., 2010). Although the average annual temperatures of Gulf of Mexico waters fluctuate around 25° C, this seemingly miniscule difference in density is important because of the oil’s very low viscosity, typical of light crude oil (Lehr et al., 2010). Fresh Macondo crude has a dynamic viscosity of 4.1 cP at 15° C, where it also exhibits non-Newtonian or shear-thinning characteristics, and after 45% evaporation increases to 85.1 cP (Lehr et al., 2010). An
important feature of MC252 ENT-052210-178 oil is its low viscosity, which does not tend to form stable water-in-oil emulsions when it is exposed and mixed with ocean water (Lehr et al., 2010). This feature was not observed during real-time MC252 wellhead discharge, where emulsification occurred as a likely byproduct of increased evaporation over a period of time and the consequent residual buildup of asphaltenes, which tend to form stable water-in-oil emulsions (Fingas et al., 2003).

4.2 Oceanic Conditions

Subsurface application of chemical dispersants was executed during the MC252 wellhead blowout as an auxiliary to surface application since it had occurred at such an extraordinarily great depth (Kujawinski et al., 2011). Due to MC252 being located nearly 1,500 m below the water’s surface, atmospheric conditions did not have much of a significant impact on dispersant fate as deep water oceanic conditions did. Conditions relating to the state of water during the subsurface application of chemical dispersants at MC252 are discussed in sections below, and include how the dispersed oil droplets enter the deepwater column, mixing energy of the deep ocean environment, salinity, and temperature of the deep water.

4.2.1 Water Column

When a deep water wellhead blowout occurs, the discharge of oil is released into the surrounding marine environment as a submerged buoyant jet (Zhao et al., 2014). Below the ocean’s surface the oil reacts with the water to form different sized droplets and bubbles at various depths in the water column, which will have notable differences in rising time due to the effects of buoyancy (Zhao et al., 2014). A concept of paramount importance is the droplet size distribution (DSD) of crude oil that is discharged from the blowout, since this distribution controls the velocity of the oil’s vertical transport as well as its quantity at any given point of the subsurface plume (Paris et al., 2012). The differences in DSD are dependent on three factors which include physiochemical properties of the discharged crude oil discussed in earlier sections, turbulent shear rate of the oil, and the temperature of water at the discharge point, both of which are discussed in the following sections (Paris et al., 2012). These factors combined with water stratification and the geographical extent of the oil spill resulted in an apparent discontinuity of
vertical DSD, which was observed in the surface and subsurface plumes of the DWH disaster (Paris et al., 2012).

Paris et al. (2012) suggested that over the course of the MC252 discharge, oil droplets > 70 µm were inclined to contribute to surface water plumes while droplets < 40 µm contributed to deep water plumes around 1,500 m. Redistribution of suspended hydrocarbon particles can potentially occur in the lower water column at depths over 1,000 m, especially if topographic conditions can foster deep water circulation processes (Paris et al., 2012). There are several studies discussed here that have attempted to simulate the transport and fate of deep water oil and gas discharges throughout the water column (Brandvik et al., 2013; Johansen et al. 2013; Paris et al., 2012; Zhao et al., 2014), and although many others exist and are currently being tested, there remains a gap in understanding which must be filled regarding various droplet formation mechanisms, especially the DSD as it relates to submerged plumes.

4.2.2 Potential Mixing Energy

Mixing energy that occurs in deep water can have profound effects on both vertical and horizontal transport of subsurface oil plumes released from wellhead blowouts and consequently affect the effectiveness of chemical dispersant application. The transport of these plumes is influenced by the synergism of oil-droplet formation by chemical dispersion and the turbulent mixing that occurs at depths where offshore oil production exists (Paris et al., 2012; NRC, 2005). At depths over 1,500 m, leaking oil is likely to be mixed with sizeable quantities of natural gas, which provides the effects of buoyancy and related fluctuations of oil droplet transport (NRC, 2005). Depending on the time of year, location of incident, and depth of discharge and dispersant application, density stratification conditions can inhibit factors of vertical mixing in the water column (Brandvik et al., 2013). This seasonal layering of water and nutrients in addition to horizontal current flows can constrain chemically dispersed oil droplets < 40 µm to deep water plumes (Brandvik et al., 2013). Laboratory experiments that aim to simulate oil breakdown and droplet formation and chemical dispersant effectiveness at the subsurface cannot entirely account for unpredictable mixing conditions present between the discharge point of a spill and the water column (Brandvik et al., 2013; Johansen et al., 2013). These experiments do maintain that deep water turbulence is the primary mechanism in oil droplet breakdown, and the
addition of chemical dispersants at depths around 1,500 m can augment the breakdown of oil droplets and constrict the DSD to deep water marine environments.

4.2.3 Salinity

As discussed in Chapter 3, the salinity of marine environments can fluctuate according to tidal flow, ocean currents, wind energy, and proximity to fresh water sources, which can all influence the mixture of fresh water with ocean water. This section focuses on the range of salinity in deep ocean water as well as the water column in which dispersed oil is transported, and how it influences the effectiveness of chemical dispersants to break down oil in deep marine waters. Ocean salinity typically increases with depth, and some cases have recorded deeper ocean waters to contain abnormally high salinity, or hypersaline concentrations (Stock et al., 2013). The experiment conducted by Tansel et al. (2014) aimed to examine the chemical dispersion of Louisiana crude oil using Corexit 9500A in marine waters that contained varying salinity and biological matter. They found the efficacy of Corexit 9500A to be significantly reduced in marine waters containing higher concentrations of salinity (30 – 50 ppt), and a relationship between dispersant: oil ratios and salinity in the Louisiana salt water environment (Tansel et al., 2014).

The experiment from Paris et al. (2012) showed that Corexit 9500A contains sulfonic acid salts and has a strong sulfonic acid-based chemical composition that increases the surface tension between oil and water. The chemical composition of Corexit 9500 suggests that it would be effective for breaking down crude oil; however, the increased salinity in a deep water environment can inhibit its effectiveness, and the presence of other water-state conditions can further complicate this relationship (Paris et al., 2012).

4.2.4 Temperature

Another deep water characteristic that relates to overall chemical dispersant effectiveness and DSD is the water’s temperature at the oil discharge point and surrounding area where dispersants are applied. A generally direct relationship exists between water temperature and depth, and studies show that the deeper the water, the colder it will be (Tansel et al., 2014). A generally inverse relationship exists between water temperature and density; as water temperature decreases, its density increases (Tansel et al., 2014). These relationships, in addition
to the likelihood of significant temperature differences throughout the point of subsurface dispersant application, water column, and the time period of a spill response, can complicate the evaluation of chemical dispersants efficacy for deep water subsurface spills (Tansel et al., 2014). The water’s temperature can influence the emulsification of oil in deep water and variations of DSD that are generated at the discharge point and throughout the water column (Paris et al., 2012).

4.3 Case Study: Deepwater Horizon (2010)

The decision to apply chemical dispersants to the deep water via subsurface injection was arguably the most controversial as well as groundbreaking decision made during the 2010 DWH incident response. Although chemical dispersants had been applied to previous oil spills that occurred below the water’s surface in shallow areas, the depth of DWH required the first subsurface application of chemical dispersants to treat underwater plumes instead of oil slicks at the water’s surface. Most background information regarding the DWH incident has previously been outlined in Chapters 1 and 3, which allows this section to focus on information regarding the subsurface application of chemical dispersants. Corexit 9500 was applied to the deep water wellhead during DWH by using a jet stream which injected it into the oil and gas discharge coming from MC252, with the intended effects to mix the dispersant evenly with the oil and gas flow into the water column (Kujawinski et al., 2011).

The mechanisms of oil transport and fate that occurred in the deep waters of the Gulf of Mexico created some difficulties for SMART teams while they determined the efficacy of injecting Corexit 9500 to disperse the surging oil (Fletcher, 2014). The high pressure and great depth at the site of the wellhead blowout had caused several physical effects on the oil as it traveled through the water column, which increased the droplet shearing, mixing energy, and water entrainment (Reddy et al., 2011). The transport of oil and associated DSD that occurred after the blowout was influenced by both the rate at which the oil rises as well as the proportion of oil that is submerged as a plume, and depended on the characteristics of the crude oil, rate of shearing, and temperature of water at the discharge point (Paris et al., 2012). Since there was a fluctuation in the pressure exerted from the surging wellhead, the jet that applied Corexit 9500 was not consistently inserted into the flow of oil and gas (Kujawinski et al., 2011). When the jet was inserted into the flow, SMART monitor teams assumed that the Corexit 9500 was being
mixed uniformly into the oil that was rising in the water column (Kujawinski et al., 2011). A diagram depicting the mechanisms of transport and ultimate fate of discharged oil from a subsurface well blowout is shown below in Figure 10.

![Diagram of oil transport and fate](image)

**Figure 10. Fate and Transport of Spilled Oil in a Deep Water Subsurface Wellhead Blowout from DWH Spill (Hazen et al., 2010).**

One of the principal objectives was to reduce the potential for further environmental injury resulting from surface oil reaching fragile ecosystems (Tamis et al., 2012). These areas consisted of wetlands and associated salt marsh and mangrove communities, fisheries, habitat that supports marine mammals, and the aphotic zone of the Gulf of Mexico where the most direct impact from uninhibited crude oil discharge had occurred (NRC, 2013). Approximately 2,900,000 L or 770,000 gallons of the total 8,200,000 L or 2,170,000 gallons of chemical
dispersants used during the DWH incident response were applied to this discharge at the subsurface, and the cumulative use of dispersants over the three month period is illustrated below in Figure 11 (Lehr et al., 2010).

![Cumulative Dispersant Use at DWH](Image)

Figure 11. Cumulative Surface and Subsurface Dispersant Use during Deepwater Horizon (Lehr et al., 2010)

Paris et al. (2012) suggested that over the course of the MC252 discharge, oil droplets > 70 µm contributed to surface water plumes while droplets < 40 µm contributed to deep water plumes at around 1,000 m. Redistribution of suspended hydrocarbon particles can potentially occur in the lower water column at depths over 1,000 m, especially if topographic conditions can foster deep water circulation processes (Paris et al., 2012). A 3D analysis representing a spatial distribution of such plumes at various depths over time is shown in Figure 12 below.
Figure 12. Time Sequence for 3D Spatial Distribution of Formation of Deep and Shallow Plumes of Oil Products from MC252 (black circle) (Paris et al., 2012).
As discussed in Chapter 3, the SMART monitoring program implemented Tier I/II/III/III+ missions during the DWH incident response (Fletcher, 2014). Tiers I/II monitoring techniques were useful throughout the surface application of chemical dispersants since Tier I required aerial observations of dispersant efficacy and Tier II required water sampling at depths of only 1 m (Fletcher, 2014). Tier III was used mostly for dispersant application monitoring for subsurface activities, and although Tier III+ missions were not included in the SMART Protocols, they served useful for advanced water sampling techniques (Fletcher, 2014). These techniques were designed to increase analytical parameters of dispersant monitoring at the subsurface, and included ship-based acoustics, LISST particle analysis, microbial analysis, dual wavelength fluorescence, dissolved oxygen, and rototox toxicity (Fletcher, 2014). BP had deployed a remotely operated vehicle to capture high-resolution footage of the oil and gas surging from MC252, and a still frame from that footage is shown below in Figure 13.

![High-resolution Still Frame of Oil and Gas Surging from MC252 at a Depth of 1.5 km (Lehr et al., 2010).](image)

Figure 13. High-resolution Still Frame of Oil and Gas Surging from MC252 at a Depth of 1.5 km (Lehr et al., 2010).
A painful lesson regarding future monitoring protocols came at a high cost during the 2010 DWH incident. The stakeholders involved throughout the interagency response effort unanimously agree that advanced techniques and monitoring capabilities should be addressed by a subsurface monitoring unit, which would deploy equipment and personnel to conduct advanced subsurface water monitoring (Fletcher, 2014).

4.4 Chapter Summary

The decision to apply chemical dispersants directly at the surging oil leaking from the MC252 wellhead was unprecedented and was essentially given validation during the chaos of one of the largest environmental disasters in modern history. The only case study discussed in this chapter was the 2010 BP DWH oil spill, since that was the only recorded subsurface application of chemical dispersants. Similar to surface application, the class of chemical dispersant to be used along with its argued effectiveness was still subject to both physical and chemical composition of the discharged oil and environmental conditions that could have altered the chemical’s ability to disperse oil in the deep ocean’s water column. These conditions include how the dispersed oil droplets enter the deep water column and are transported vertically or horizontally, mixing energy of the deep ocean, salinity fluctuations with water depth, and temperature of the deep water. SMART monitoring and observations during the first few days following subsurface injection of Corexit 9500 did not provide conclusive data regarding the effectiveness of subsurface injection (Lehr et al., 2010). After the first day of dispersant application, the layers of crude oil had appeared to thin, but the next day the layer reverted back to the form that it had initially been (Lehr et al. 2010). This phenomenon was likely instigated by the fluctuating vertical transport of the oil and the changes in DSD, which then produced observable differences in both surface water oil slicks and subsurface plumes (Lehr, et al., 2010). Chapter 5 will transition to assess various ecosystem impacts associated with both surface and subsurface application of chemical dispersants based on all case studies discussed earlier.
CHAPTER 5 – ASSESSMENT OF ECOSYSTEM IMPACTS

After an oil spill incident occurs in the marine environment, the RRTs must prioritize response strategies and adapt to the spill dynamics that are taking place. The first response option is the containment and management of the oil that has already been discharged. The purpose behind this action is to minimize and prevent further damage that could be inflicted onto the marine ecosystem and local organisms. If mechanical recovery is insufficient or ineffective in corralling and removing spilled oil, another response option is the application of chemical dispersants that can break oil down into smaller, supposedly less harmful droplets, according to the NCP (40 C.F.R. §300.910). This is a controversial method that has primarily been used to treat oil slicks on the water’s surface, but has been used to treat the subsurface MC252 oil well discharge during the DWH disaster (Spier et al., 2013).

The application of chemical dispersants is controversial because of the challenges that relate to evaluating environmental tradeoffs associated with their use. Over the past several decades the dispersant themselves have evolved into far less toxic formulations than had previously been used during spill response. However, even though the chemicals used today have succeeded in effectively dispersing oil in surface spills and in laboratory experiments, conflicting research and data continue to circulate in the scientific community relating to potential ecosystem impacts that stem from chemical dispersants and dispersed oil. This chapter examines various trophic-level marine ecosystem impacts associated with surface and subsurface dispersant application that have been studied either in laboratory experiments or in the field after oil spill incidents discussed throughout this research. The primary concern of the ecosystem analyses within this research are potential toxicological responses that could cause injury to special-status, indicator, or keystone species, as well as impacts to trophic structures which could lead to long-term or large-scale consequences. Variations in toxicological responses can occur depending on the grade and quantity of oil spilled, class of chemical dispersant used, time of exposure, and individual responses from the marine organisms that are exposed to spilled oil, dispersed oil, and chemical dispersants (Chang et al., 2014). A major issue in modern studies is the actual toxicity of chemically dispersed oil in comparison to physically dispersed oil, both in surface and subsurface waters, and the range of findings in the toxicological effects to various marine organisms are listed below in Table 9 (Fingas, 2014).

<table>
<thead>
<tr>
<th>Species or Class</th>
<th>Effect of Dispersants</th>
<th>Author</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlantic herring embryos</td>
<td>same at same concentration</td>
<td>Adams et al.</td>
<td>2014</td>
</tr>
<tr>
<td>Rabbit fish</td>
<td>100-fold more toxic</td>
<td>Agam et al.</td>
<td>2013</td>
</tr>
<tr>
<td>Rabbit fish</td>
<td>slightly more</td>
<td>Agam et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Rabbit fish</td>
<td>same</td>
<td>Agam et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Microzooplankton</td>
<td>significantly increased</td>
<td>Almeda et al.</td>
<td>2014</td>
</tr>
<tr>
<td>Copepods</td>
<td>1.6 times more toxic</td>
<td>Almeda et al.</td>
<td>2014</td>
</tr>
<tr>
<td>Mexo zooplankton</td>
<td>2.3 to 3.4 times more toxic</td>
<td>Almeda et al.</td>
<td>2013</td>
</tr>
<tr>
<td>Juvenile mud crabs</td>
<td>significantly increased</td>
<td>Anderson et al.</td>
<td>2014</td>
</tr>
<tr>
<td>Spotted sea trout</td>
<td>larval more, juvenile less than high mixing</td>
<td>Brewton et al.</td>
<td>2013</td>
</tr>
<tr>
<td>European sea bass</td>
<td>lowest growth rate of all types of exposures</td>
<td>Claireaux et al.</td>
<td>2013</td>
</tr>
<tr>
<td>Marine copepod</td>
<td>same but dispersant alone shows more lethality</td>
<td>Cohen et al.</td>
<td>2014</td>
</tr>
<tr>
<td>Tambaqui - tropical fish</td>
<td>dispersant and CEWAF causes impairment to gill ion regulation</td>
<td>Duarte et al.</td>
<td>2010</td>
</tr>
<tr>
<td>Arctic marine amphipod</td>
<td>dispersants decreased lysosomal stability</td>
<td>Faksness et al.</td>
<td>2011</td>
</tr>
<tr>
<td>Mallard duck eggs</td>
<td>variable but dispersant appeared to increased transference of compounds into eggs</td>
<td>Finch et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Marine plankton</td>
<td>little effect</td>
<td>Gao et al.</td>
<td>2014</td>
</tr>
<tr>
<td>Coral larvae</td>
<td>CEWAF led to less settlement and Dispersant alone to least settlement</td>
<td>Goodbody-Gringley et al.</td>
<td>2013</td>
</tr>
<tr>
<td>Northern algae and copepods</td>
<td>dispersants toxic</td>
<td>Hansen et al.</td>
<td>2014</td>
</tr>
<tr>
<td>Copepod</td>
<td>increased toxicity at low levels, decrease at high levels</td>
<td>Hansen et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Shrimp and silverside</td>
<td>dispersant alone slightly toxic, same as mixture</td>
<td>Hansen et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Diatom</td>
<td>exposure to dispersants or DEWAF caused membrane damage</td>
<td>Hemmer et al.</td>
<td>2011</td>
</tr>
<tr>
<td>Genotoxicity and endocrine disruption</td>
<td>only very little toxicity noted with some products</td>
<td>Hook et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Estuarine fish</td>
<td>dispersant exponentially increased PAH concentrations, CEWAF more toxic than WAF</td>
<td>Kuhl et al.</td>
<td>2013</td>
</tr>
<tr>
<td>Pelagic tunicates (zooplankton)</td>
<td>dispersant increased ingested oil, but this was eliminated via faecal pellets</td>
<td>Lee et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Pacific Oyster</td>
<td>immune and detoxification affected negatively by chemical dispersants</td>
<td>Luna-Acosta et al.</td>
<td>2011</td>
</tr>
<tr>
<td>Mullet</td>
<td>about the same toxicity</td>
<td>Milinkovitch et al.</td>
<td>2013</td>
</tr>
<tr>
<td>Mullet</td>
<td>about the same toxicity</td>
<td>Milinkovitch et al.</td>
<td>2012</td>
</tr>
<tr>
<td>Fish, L. ramada</td>
<td>CEWAF more toxic</td>
<td>Milinkovitch et al.</td>
<td>2011</td>
</tr>
<tr>
<td>Mullet</td>
<td>dispersant application likely to impair cardiac function</td>
<td>Milinkovitch et al.</td>
<td>2013</td>
</tr>
<tr>
<td>Arctic cod</td>
<td>dispersants do not appear to have transcriptional effect</td>
<td>Olsvik et al.</td>
<td>2012</td>
</tr>
</tbody>
</table>

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

5.1 Surface Application

The purpose of applying chemicals to surface waters of a marine ecosystem during an oil spill incident is to disperse the surface slick into the water column. Surface application of dispersants is intended to reduce potential adverse impacts to the surrounding ecosystem by removing visible oil from the water’s surface where marine mammals and sea birds frequently pass through to breath and forage (Chang et al., 2014). Another objective is to minimize exposure pathways to vulnerable coastal shores, which consist of both intertidal zones and sandy beaches which provide refuge for nesting, breeding, and foraging marine organisms (Kappell et al., 2014). The ecosystems that are examined in the following sections are located in the Gulf of Mexico and off the Alaskan Coast. A great deal of controlled laboratory research has been dedicated to simulating field experiments for surface oil spills to test toxicological responses among aquatic organisms; however, it is extremely difficult to account for the variety of
parameters that exist in an actual oil spill incident. The reoccurring point made throughout this research has indicated how many factors are related to the efficacy of chemical dispersant application. To reiterate, these factors include the characteristics of oil spilled, present mixing energy, and state of the water, which all serve important functions in either enhancing or inhibiting the formation of ideally sized oil droplets to disperse into the water column.

5.1.1 Effects on Trophic Structure

Although there is an overwhelmingly greater amount of research available related to surface rather than subsurface application of chemical dispersants, controversy remains over their potential ecosystem impacts and environmental tradeoffs associated with their use. A majority of the studies performed on evaluating impacts of surface application of dispersants on the marine trophic structure focused on lethal effects instead of broader impacts, such as impairment to metamorphic success, reproduction, and other population dynamics (Almeda et al., 2014b). Among these studies, there is a range of data in disagreement regarding the extent of marine species’ toxicological responses, based on either the existence of data that used outdated dispersant products, or the inconsistent controlling factors of each study’s laboratory exposure to chemical dispersants or dispersed crude oil.

According to laboratory experiments conducted by George-Ares and Clark (2000), the application of two commonly used chemical dispersants Corexit 9500 and 9527, both of which were used individually or cooperatively in all case studies discussed earlier, resulted in a low to moderate toxicological response from most aquatic species tested. In opposition, Almeda et al. (2014a) found a significant reduction in survival and growth rates of planktonic larvae or meroplanktonic that were exposed to Corexit 9500 and its dispersed oil at concentrations determined to be similar to those that would be present in the water column after Corexit 9500 application during an actual oil spill. In the same study they also observed a high possibility for the biotransfer of petroleum hydrocarbons throughout the coastal pelagic ecosystem, from the lower-trophic levels of planktonic larvae to higher-trophic level marine benthic invertebrates. A 2000 study from Wolfe et al. had examined the tropic transfer and bioavailability of the crude oil compound phenanthrene, with characteristics of not being easily soluble in water and tending to bioaccumulate, to marine algae and rotifers.
5.1.2 Effects on Overall Ecosystem

Although the marine resources discussed throughout this research relate to their respective geographical regions, there is a much greater number of species affected that are beyond these regions. The scope of environmental impacts should consider the range of life-cycle activities that crude oil and associated petroleum products have. With that said, the marine species that are at-risk or have already been impacted in waters off the Gulf of Mexico or Alaska due to surface application of dispersants are examined in this section.

Similar to all other ecosystems, the effects of chemical dispersants and chemically dispersed oil on the Arctic marine ecosystem are influenced by the oil characteristics, concentrations of oil and dispersant, oceanic and atmospheric conditions, and species that are exposed (Hsiao et al., 1978). Although the effectiveness of chemical dispersants are difficult to predict under subarctic conditions, Moles et al. (2002) found that weathering, temperature, and salinity were the most important factors in evaluating dispersant performance. In subarctic marine waters that have lower temperature and salinity, Moles et al. (2002) found that emulsification actually enhanced the efficacy of Corexit 9500 and 9527 on dispersing Alaska North Slope crude oil. This is significant because emulsified oil is typically considered to contain the most toxic properties of spilled oil, relative to fresh and weathered oil (Moles et al., 2002).

The Gulf of Mexico is an extremely vulnerable ecosystem due to the sensitive natural resources and the high concentration of large-scale petroleum operations that are located within its area. Coastal wetland ecosystems have been declining at exponential rates across the U.S., and almost half of the remaining wetlands are located within the Gulf of Mexico (NRC, 2013). Louisiana owns approximately 40% of this share, and unfortunately these areas are standing targets in the event of large-scale oil or hazardous material spills (NRC, 2013). Wetland ecosystems consisting of salt marsh and mangrove communities serve dynamic roles in stabilizing coastlines and regulating nutrient-cycles and water quality (Pietroski et al., 2015). Nearly 1,770 km of salt marsh wetlands which were located just 64 km from MC252, were impacted during DWH (NRC, 2013). The acute exposure of crude oil and chemically dispersed oil to coastal salt marshes in the Gulf of Mexico during DWH could result in long-term impairment of vegetation (NRC, 2013).
Exposure of crude oil by itself can be toxic to marine vegetation when it coats leaf surfaces and plant roots (Pezeshki et al., 2001). The NRC (2013) report cited various studies that found if root structures survived the initial toxic exposures from MC252 oil, they may be able to recover on their own, whereas if their root structures were damaged or destroyed, they would not be able to recover. The death of marshland vegetation due to root structure loss has resulted in the conversion of coastal marshlands to less productive open water habitats (NRC, 2013). To exacerbate the DWH incident, Tropical Storm Alex was upgraded to hurricane status on June 29th, 2010, and generated waves that transported weathered oil to coastal marshes and caused additional erosion (NRC, 2013).

Evaluations for phytotoxicity or toxicological effects caused by chemical dispersants and dispersed oil in the water column and on substrate for plant growth have largely been drawn from research conducted after actual oil spill incidents in marine environments (Lewis and Pryor, 2013). Generalizations concerning phytotoxicity are challenging to predict due not only to most plant and dispersant data from testing being outdated, but also the uneven range of reported concentrations (Lewis and Pryor, 2013). Most acute phytotoxic effect concentrations for salt water plants have been upwards of 10 parts per million (ppm), representative of a slight toxicity, but are considered to be relatively tolerant towards the effects of chemical dispersants on the NCP Product Schedule and dispersed oil (Lewis and Pryor, 2013). With that said, there are still many questions unanswered pertaining to the phytotoxicity of dispersants and dispersed oil to both salt and freshwater plants, especially if surface application of dispersants is required near intertidal, subtidal, and other diverse ecosystems.

5.2 Subsurface Application

Chemical dispersants had been injected directly to the massive underwater plume discharged from MC252, with the intention of reducing the interfacial surface tension between the deep water and oil so that the oil compounds would break down into smaller droplets and dilute vertically and horizontally into the water column (Kujawinski et al., 2011). Because this was a revolutionary technique, no data had existed on its effectiveness, transport of chemical dispersants, or potential adverse impacts to the surrounding deep water marine ecosystem. Several studies have examined the initial sizes of oil droplets and their evolution over time and argue that the great depth and high pressure circumstances of the MC252 well blowout resulted
in forming oil droplets that were already neutrally buoyant, and the subsurface application of Corexit 9500 only formed smaller oil droplets that recirculated to form separate deep water plumes (Kujawinski et al., 2011; Paris et al., 2012; Zhao et al., 2014). The driving force of the formation of these plumes is called a fold-out, and is the result of the chemical changes that occurred from dispersant solubility within methane and water (Fingas, 2014). The presence of ultra-fine oil droplets with the supplement of horizontal transport could potentially have redistributed these suspended oil droplets and other oil particulates throughout the lower sections of the water column as well as the euphotic zone, which receives enough sunlight to permit photosynthesis (Paris et al., 2012).

Dioctyl sulfosuccinate (DOSS) is a primary component in the formulation of Corexit dispersants, and when broken down in water has been found to have aquatic toxicity levels twice that of the Corexit dispersant by themselves (Gray et al., 2014). In May and June of 2010, Kujawinski at al. (2011) measured DOSS concentrations at various water depths (10 – 1,300 m) and distances from MC252 (0.58 – 1.9 km) from two vessels and found that refractory DOSS compounds persisted in deep water plumes at depths up to 1,100 m in concentrations of 1 – 10 µg/L. These concentrations are typically lower than those that are tested in published toxicological response studies, even though such research on deep ocean biota is unprecedented in current studies of this nature (Kujawinski et al., 2011). However, in September of that year, DOSS concentrations at the same locations were 2 – 3 orders of magnitude smaller than those detected in May and June (Kujawinski et al., 2011). Although it is possible for biodegradation and sedimentation to be factors in reducing DOSS concentration in water bodies, Kujawinski et al. (2011) concluded that dilution was the primary mechanism for this reduction. DOSS compounds were observed to dissolve during vertical transport and become detained in these plumes through partitioning with methane, water, and gas hydrate phases (Kujawinski et al., 2011). Because of these subsurface intrusions hydrocarbons, methane, and dispersant compounds, a probability exists that local marine organisms and surrounding ecosystems could be adversely affected.

5.2.1 Effects on Trophic Structure

In relatively shallow marine environments, microbial communities are capable of digesting petroleum hydrocarbon compounds and contribute to pollution discharge remediation
(NRC, 2013). The aphotic zone that supports deep water microbial communities was studied near MC252, and observed to have digested crude oil and gas during its transport through the water column (NRC, 2013). There were variations in the rate of vertical transport of dispersed oil due to reductions of pressure from MC252, which had: 1) reduced the velocity of particle transport; and 2) dissipated energy through water entrainment and particle transfer into the water column (Fingas, 2014). At this point, the vertical and horizontal transport of oil varied, and resulted in the formation of discrete plumes containing weathered and emulsified oil with varying particle sizes (Fingas, 2014). The presence of these plumes with different oil droplet particle sizes at varying depths could have taken a long time to rise to the water’s surface, and remained within the water column to be potentially be absorbed by marine organisms (Fingas, 2014).

An important characteristic of the Macondo crude oil is its composition of light, readily biodegradable hydrocarbons (Atlas and Hazen, 2011). Within the main deep water plume the density of biodegrading bacterial cells was significantly higher at $5.51 \times 10^4$ cells per milliliter (cells/mL) than outside of the plume at $2.73 \times 10^4$ cells/mL (Hazen et al., 2010). These measurements were recorded approximately 5 – 7 weeks from the beginning of the MC252 wellhead blowout (Hazen et al., 2010). According to the NRC (2013) report, microbial respiration of propane and ethane accounted for approximately 70% of depleted oxygen in the subsurface plume.

5.2.2 Effects on Overall Ecosystem

Deep water communities in the aphotic zone where the MC252 wellhead blowout occurred were the most vulnerable to potential adverse impacts from the discharged oil, Corexit 9500 that was injected, and the chemically dispersed oil. The aphotic zone in the Gulf of Mexico replenishes nutrients in the photic zone depleted via photosynthetic activities, and is vital to overlying organisms for nutrient-cycling (Pietroski et al., 2015). As dispersant pathways of sedimentation, bioaccumulation, and biodegradation vary, they can influence species of varying trophic levels that are exposed to them (Fingas, 2014). Even though it has been five years since DWH, the lack of understanding regarding the deep waters of the Gulf of Mexico and findings that draw definitive results for overall ecosystem impacts raise serious concerns about potential
future incidents, and the requirement for additional research to address subsurface fate of chemical dispersants.

Table 9 listed 42 toxicological studies, most of which were inspired by the 2010 DWH disaster, which examined impacts to marine species ranging from microbial organisms, invertebrates, fish, birds, and plants (Fingas, 2014). The general findings from these studies appeared to be variable, even though there were observable patterns, which depended on the controlling factors of the study, the species involved, life stage of that species, and the conditions regarding the exposure to chemical dispersants and dispersed oil. A pivotal finding that corresponds with many of the studies presented in Table 9 is that the toxicity of chemically dispersed oil is generally higher than the toxicity of the dispersant by themselves. Since the only instance of deep water subsurface injection of chemical dispersants was during the 2010 DWH disaster, substantial studies that examine ecosystem impacts concerning this type of response are in their stage of bourgeoning. With that said, the variety of conditions that exist in a deep water wellhead blowout can influence the formation of dispersed oil droplets and the ability of benthic marine organisms to bioaccumulate these potentially toxic droplets (Kujawinski et al., 2011).

One noteworthy contradiction present in Table 9 is the variation of toxicological responses from chemical dispersants that were found in rabbit fish studies conducted by Agamy (2012a; 2012b; 2013). The Agamy (2012a) study found that there were no adverse toxicological effects to rabbit fish resulting from exposure to chemical dispersants, whereas the Agamy (2012b) study found that there was indeed some toxicological effect that resulted from exposure. Findings from the Agamy (2013) study strayed much further from the previous two, and concluded that under the same exposure of rabbit fish to chemical dispersants, the toxicological response increased 100 fold. These conflicting results highlight the need to not only invest more into toxicological response research from chemical dispersant exposure, but also manage both field studies and controlled laboratory settings such that data and results can be most precise. Additional considerations that must be taken into account are the challenges presented when simulating field conditions for certain species within laboratory settings, and attempting to find definitive conclusions that can influence recommendations for toxicological exposure.
5.3 Chapter Summary

Perhaps one of the most controversial parameters regarding the surface and subsurface application of chemical dispersants are their potential effects on the trophic structure of the marine environment and surrounding ecosystem impacts. The effects of chemical dispersants and chemically dispersed oil on ecosystem are influenced by the oil characteristics, concentrations of oil and dispersant, oceanic and atmospheric conditions, and species that are exposed (Hsiao et al., 1978). This argument is more valid for subsurface application for oil discharge incidents into deep water marine environments, where the physical conditions of a wellhead blowout are difficult to predict in controlled laboratory settings. The following chapter outlines conclusions drawn from this research based on the extensive government and academic sources that have contributed to the studies of surface and subsurface application of chemical dispersants.
CHAPTER 6 – RESEARCH CONCLUSIONS

This research focuses primarily on the evolution and application of chemical dispersants in surface and subsurface oil spills with associated ecosystem impacts, while identifying other limiting factors related to their use. These factors mostly rely upon the region in which the spill occurred, and include the oceanic and atmospheric conditions, severity of the spill, and political structure. The conclusions and findings presented here are an analytical synthesis of peer-reviewed articles and government reports. However, many of these articles and reports are contradictory, and arguments concerning the efficacy of chemical dispersants and the toxicity of dispersants and dispersed oil are controversial at best.

The ability of a modern, commercially available chemical dispersant to be effective in breaking down oil droplets to ideal sizes for dilution and biodegradation has been proven both in real-time emergency application and in controlled laboratory settings. The parameters that can and will complicate this baseline success are the environmental conditions pertaining to surface and especially subsurface spills. If the oceanic and atmospheric conditions permit the surface application of chemical dispersants during an oil spill, this method has typically been successful in its goal – dispersing large surface slicks into relatively smaller oil droplets that dilute into the water column. In the case studies examined throughout this research, surface application had generally been successful in the breakdown of spilled oil except in the Exxon-Valdez tanker spill, where a storm disrupted dispersant application activities. Concerning subsurface application, several experiments supported the hypothesis that the great depth and high pressure of the MC252 wellhead blowout caused the subsurface oil to break down into ultra-fine particulates that could be absorbed by the immediate marine community (Kujawinski et al., 2011; Paris et al., 2012; Zhao et al., 2014). There are considerable limitations that exist with surface and subsurface application of chemical dispersants, and ongoing research that both supports and challenges the validity of their use.

6.1 Surface Application

The controversy regarding the application of chemical dispersants to surface waters does not concern the ability to break down the oil slick into droplets, but rather the potential toxicological effects that the dispersant and varying sizes of dispersed oil droplets entering the
water column could have on the surrounding ecosystem. Under the right conditions related to the window of opportunity, mixing energy, and oceanic and atmospheric conditions, applying dispersants to surface water oil slicks can be effective in preventing the transport of the slick towards vulnerable shorelines to inflict further injury. If weathering occurs during the first 24 – 48 hours after the spill, and the oil spilled contains simultaneous fractions of both asphaltenes and paraffins, stable water-in-oil emulsions or mousse will likely form at the water’s surface. Emulsification or formation of mousse increases the viscosity of the spilled oil and therefore reduces its ability to be chemically dispersed. By increasing the ratio of surfactant in the chemical dispersant formulation, water-in-oil emulsions can be destabilized when those surfactants transfer the original surfactants from the interface (NRC, 1989).

It is argued that the operational evolution of policy, technology, training, and resources used during surface application of chemical dispersants for oil spills that spanned during the last half-century has allowed responders to use dispersants effectively so that affected communities and ecosystems could heal faster than they would without dispersants (Tamis et al., 2012). SMART Protocols and the three-tiered systems that are in use for surface spills contain adequate dispersant application monitoring requirements (Fletcher, 2014). With that said, even though the systematic framework is in place, it has not necessarily been followed through to realize its potential during actual oil spill incidents, such as those discussed in this research. As described in the Poseidon Pipeline Spill (2000), Eugene Island Spill (2009), and the DWH (2010) case studies, there were significant gaps in communication and SMART Protocols between levels of the unified command, which led to lapses in recording data during monitoring activities and reporting this data throughout the ICS (Stoermer et al., 2001; USCG, 2009; Fletcher, 2014). Based on these documented errors during crucial points in emergency oil spill response, and in order for the current protocols to enhance the effectiveness of surface application of chemical dispersants, there must be substantial improvements made regarding accountability, communication, and monitoring.

Laboratory testing and results derived from case studies have indicated the ability for dispersants to enhance the process of oil sedimentation when applied at the water’s surface (Almeda et al., 2013). In turn, this dispersed oil could result both in more persistent toxicity to marine benthic organisms and also a decrease in the rate that sedimentation occurs (Sun et al., 2012). Other opposite effects that have been perceived during surface application relate to the
degradation of chemically dispersed oil. The current ratio of scientific literature is split into approximate thirds regarding the effects of chemical dispersants on biodegradation, and these are listed below in Table 10 (Fingas, 2014). Some studies observed that when applied at the water’s surface, chemical dispersants can enhance the rate of biodegradation into the water column, whereas others found no differences in the rate (Tamis et al., 2012). In general, studies citing a direct relationship between chemical dispersants and oil biodegradation found that the dispersed oil becomes more available to biodegrading microorganisms due to the increase in oil and water surface area relative to the size of the organisms (Fingas, 2014). The results from more recent studies found that dispersants actually inhibit the process of oil biodegradation because of two reasons. First, microbial growth is stagnant in open oceans where surface slicks can occur due to limited nutrients, which hinders surfactant effectiveness and produces water-in-oil emulsions (Fingas, 2014). The second reason is the inability of chemical dispersants to biodegrade PAHs into the marine environment (Fingas, 2014).


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

In 2010, one of the most complex and challenging environmental disasters in modern history occurred during the DWH MC252 wellhead blowout. Although it has currently been 5 years since this disaster, deep water subsurface application of chemical dispersants persists as a method of unknown effectiveness and biological consequences. The regulatory framework in place at that time was not appropriate to respond adequately to a deep water spill, and since then all stakeholders have advocated changes to SMART Protocols to address subsurface dispersant injection. Similar to surface application of chemical dispersants, subsurface deep water and mixing conditions have tremendous influence on the transport and fate of spilled oil and dispersed oil.

In preparing the Final Report for DWH, the original intent of the SMART Protocols was considered to be adequate for “typical” chemical dispersant operations, defined as those that span a limited geographical region and last up to several days (Fletcher, 2014). It was concluded that the scope and intent of the SMART Protocols had not provided adequate dispersant monitoring requirements for a deep water spill having the severity of the MC252 wellhead blowout in 2010 (Fletcher, 2014). Since the protocols, training, and equipment of SMART teams were geared towards surface dispersant application and monitoring the water column to approximately 10 m in depth, there were staggering differences in the monitoring efforts at the water’s surface and subsurface (Fletcher, 2014).

During the DWH spill, components of the deep water microbial community were altered, including its size and composition, when the microbes responded to the chemically dispersed oil as well as the surging oil which formed underwater plumes (Atlas and Hazen, 2011). The various mixing processes at MC252, including pressure, buoyancy, and horizontal currents, recirculated the deep water plume that contained microbial oil degraders and caused the accelerated biodegradation of the suspended dispersed oil particles (NRC, 2013).

6.3 Limitations of Research

Limitations of this research are not confined to the understanding of toxicological effects and circumstantial efficacy of chemical dispersants for treating oil spills, but also expand to the management response techniques and monitoring systems which influence many dynamics of dispersant application. The inability to successfully draw parallels between findings of
Experimental testing and oil spill incidents has promoted a deficiency in the understanding of chemical dispersant effectiveness and possible negative implications. The controversy that exists with the lack of understanding presents an even bigger challenge to policy-makers and response organizations. This figurative gap of agreement between scientific support and actual incident response data further prolongs the process of effective governmental oversight when it comes to regulating the approval of chemical dispersant use and monitoring their application.

Even with a combined international effort to study chemical dispersant application at the water’s surface and subsurface, tangible effects of chemical dispersants on the properties of oil droplets, interactions between oil and sediments, and the transport and fate of spilled oil in the marine environment are not adequately understood to the point of consistent agreement (Tamis et al., 2012). The extrapolation of results from controlled laboratory experiments to actual large scale oil spills or blowouts is uncertain, and such large scale laboratory or field simulations of spill incidents may be too costly to perform or have limits in their scope (Brandvik et al., 2013). One of these limitations occurred during a controlled field simulation of deep water oil discharge incidents by Zhao et al. (2014), where the dispersed oil was represented by steady-state or equilibrium values, and did not quantify any variations in evolution of oil droplet sizes or DSD during vertical and horizontal transport from the oil discharge point and throughout the water column. Zhao et al. (2014) attempted to calculate the evolution of DSD by developing a numerical model (VDROP-J), even though the formulas that were applied were purely empirical and did not consider external controlling factors that could potentially exist in a deep water wellhead blowout and influence the DSD in a submerged buoyant jet.

In conclusion, the inability to simulate all conditions within a marine environment in which a spill occurs, either surface or subsurface, presents challenging obstacles for implementing emergency response strategies which could result in lesser overall environmental impacts. Furthermore, the lack of tangible data that existed before DWH on subsurface dispersant use and the inconclusive data that exists today regarding its efficacy and ecosystem impacts simply perpetuates the opaqueness of subsurface application and the need for further research to evaluate its use. The next chapter covers several management recommendations that could be implemented to improve current response strategies for oil spill incidents and chemical dispersant application as well as strategies that are aimed at reducing the possibility of an oil spill incident from occurring.
The objective of this research was to describe the complex dynamic of chemical dispersant use, while drawing parallels between the regulatory structures governing their use, their application to surface and subsurface waters, and potential ecosystem impacts. The efficacy of dispersant use has been more transparent during application to surface spills than subsurface spills due to the overwhelming number of cases and research which supports that claim. However, the ability of chemical dispersants to break down oil into dispersible droplets that dilute into the water column is heavily dependent on external conditions that can either enhance this process or support its failure. The oil spill incidents that have occurred throughout the past several decades and mistakes made in cleaning them up have provided painful yet valuable lessons on how to respond to future spill disasters more efficiently and effectively. Environmental regulations and monitoring programs have evolved to adapt to mistakes made in the past, and continue to do so with additional painful lessons and research that can provide insight on the various conditions in which chemical dispersants react with spilled oil and how responders can counter such conditions. Even though the course of nature cannot be controlled or changed, management strategies that are aimed at reducing the risk of oil exposure to the marine environment can be adopted. Also, efforts enhancing the current strategies of oil spill response, improving incident command structure and monitoring programs, and continuing research to evaluate the ultimate fate of chemical dispersants and dispersed oil in the marine environment are warranted.

7.1 Existing Response Methods

Response methods for oil spill incidents that exist today are a direct result of lessons learned from past oil spill incidents and collaborations geared towards more successful chemical dispersant response. One example of a continually evolving regulation is the NCP, which was developed in 1968 and implemented the first comprehensive incident response system. A model of the National Product Schedule was first introduced in 1982 to list chemical dispersants that are approved for use in U.S. waters, and is updated on an as-needed basis to add or remove chemical dispersants, with the most current being from December of 2014. The SMART Protocols were first developed by a convention of federal response agencies in 1997 and were
then restructured in 2006 in order to improve the monitoring of response technologies used when applying dispersants during oil spills into marine environments. Yet, in the 2010 DWH disaster, significant gaps were exposed in the SMART Protocols related to monitoring subsurface dispersant application, and it is highly recommended that a supplementary document be developed for monitoring subsurface dispersant injection.

Even though this regulatory framework exists and is supposed to facilitate an effective emergency response to an oil spill, responses are seldom executed flawlessly due to the potential for a wide variety of human error or equipment malfunction. Other unpredictable circumstances such as inclement weather or unique spill circumstances can also negatively affect the success of an oil spill response. The primary recommendation arising from this research that concerns the existing emergency response strategies and monitoring programs is to reinforce them. This reinforcement expands from the resources and personnel available during the response to communication throughout the Incident Command Structure (ICS). In regions where a pre-authorization agreement permits the application of chemical dispersants, it would be valuable to the relatively small time window for dispersant use to increase the number of staging areas that contain oil spill response equipment. This equipment consists of aircraft such as helicopters and planes, small marine vessels that are fitted with dispersant spraying systems, and a routinely maintained stockpile of approved chemical dispersants.

The personnel whom are required to be readily available are specially trained aircraft pilots and marine vessel captains that command support crews which direct the extent and volume of dispersant application from aerial view, operate dispersant spraying equipment, recover damaged natural resources or injured wildlife, and monitor the instant effects of the chemical dispersant application. All of these support personnel should be required to record their activities and any changing circumstances during the spill response that could hinder its progress, as per the revised 2006 SMART Protocols. Communication throughout the incident command structure can be improved by bridging gaps and lapses in SMART practices that had previously occurred during the oil spill responses discussed throughout this research. The failure of response personnel to constantly record conditions during chemical dispersant application and report the efficacy of response technologies is a relatively resolvable issue, and comes down to propagating accountability throughout the ranks and utilizing experienced managers with high expectations for closely following procedures. Management decisions can be challenging due to
the conflicting and contradicting scientific research regarding the efficacy and toxicological impacts of chemical dispersants; however, the ability of unified command to function as a cohesive and functional unit plays no part in this scientific controversy and should not in itself deter the success of an oil spill response including dispersant application.

7.2 Future Operations

Aside from improving the current structure that exists in response methodologies, steps can be taken to both reduce the risk of oil spill incidents and improve understanding of the relationship between chemical dispersants and spilled oil in marine environments. It is no national secret that the continued operation of the existing infrastructure, at least in the foreseeable future, relies heavily upon the extraction, transportation, and combustion of fossil fuels, particularly crude oil and associated petroleum products. The scale of these operations is not dwindling, and the thirst for crude oil has lead companies and government to near desperation on where extraction occurs. Even with the small safety net that emergency response tactics provide, society is still perpetuating damages that stem from the life cycle of crude oil, and by continuing to mine and transport oil to and from the furthest reaches of the planet, the potential for risk of spills and environmental injury is as high as ever.

One facet of extraction in the life cycle of crude oil that can be regulated more stringently is the phase in which oil and natural gas exploration and drilling operation permits are administered to companies that mine them. The reality is that oil located in easily accessible reservoirs is being or has already been exhausted, so exploration for oil reserves is occurring deeper below the Earth’s surface and in more remote areas where drilling had previously been impractical due to industrial limitations and environmental concerns. It is not reasonable to believe that oil extraction and consumption will cease indefinitely while it still an accessible commodity or while existing infrastructure depends on it. A more reasonable goal is to consider limiting oil exploration and drilling in areas of environmental concern, such as deep offshore waters, regions in close proximity to drinking water, and ecosystems containing sensitive wildlife or economic interests. Policy-makers must address the outstanding risks associated with extracting crude oil in these areas, and assess the benefits that could come from accepting those risks. As mentioned in the previous chapter, laboratory or field experiments attempt to find definitive results by simulating deep water oil spills and testing reactions with various biota that
could be present during such a spill. It was concluded that extensive limitations exist with these simulations, and investing more research in determining how deep water or other non-traditional environments affect hydrocarbon dispersion and where accidental discharge is a concern, can influence the decision for regulators to issue exploratory or drilling permits in these areas.

7.3 Alternatives

A final scenario to consider when responding to an oil spill incident is one which does not involve the use of chemical dispersants. Figure 2 from Chapter 2 illustrated the decision-making process for when to use chemical dispersants or when to opt for focusing on mechanical recovery. Other than chemical dispersion or mechanical containment and recovery, additional methods include in-situ burning, utilizing biosurfactants, microbial degradation, and natural dispersion or no response. This section focuses on the methods of applying biosurfactants and natural dispersion.

Although research is conflicting and findings are inconclusive, the unique properties of biosurfactants or microbial surface active agents have been considered as a complement to or even a replacement for chemical dispersants during an oil spill response (Kosaric, 1992). There are several processes which are attractive for these commercially-produced agents to work in conjunction with marine microbial communities that could enhance the biodegradation of crude oil and associated TPHs. To begin with, biosurfactants act as agents that facilitate the contact between bacterial cells and hydrophobic oil hydrocarbons (Matvyeyeva et al., 2014). Their argued biodegradability and relatively low toxicity compared to chemical dispersants presents a case for considering their functionality in oil spill remediation (Kosaric, 1992). Kosaric (1992) also determined that when bacterial cells come in contact with hydrocarbon compounds, they have the ability to enhance de-emulsification by destabilizing oil-in-water and water-in-oil emulsions. The commercial success of biosurfactants is still limited by their high production costs and general consensus over their efficacy is attributed to a lack of control over the targeted oil spill areas in which they are applied, since varying environmental conditions directly affect the ecosystem impacts of biosurfactants (Matvyeyeva et al., 2014).

The application of chemical dispersants can be assumed to facilitate or enhance conditions for marine microbial community growth and oil biodegradation for two reasons. First, the chemical dispersion of spilled oil reduces the interfacial surface tension between water
and oil to form smaller droplets (NRC, 1989). The second reason is the degradation of these droplets taking place at the oil-water interface, which could potentially increase the rate of biodegradation (NRC, 1989). Sand microbial communities have a central role in nutrient cycling throughout coastal marine ecosystems (Kappell et al., 2014). Microorganisms that inhabit these communities are known to be early responders to anthropogenic pollution, particularly oil spills, by degrading and decomposing oil hydrocarbons (Kappell et al., 2014).

Lu et al. (2012) analyzed various sea water samples from DWH using a functional gene microarray, or “GeoChip,” to evaluate the effects of the marine microbial community on hydrocarbon degradation in the deep water plume. Their results indicated that aerobic and anaerobic degradation of oil hydrocarbon components occurred through numerous functional genes and microbial populations (Lu et al., 2012). Based on their results from the DWH seawater samples, Lu et al., (2012) concluded that there is high potential for oil hydrocarbon degrading microbial populations to conduct in situ bioremediation of deep water oil plumes which could have a significant influence on the transport and ultimate fate of subsurface oil spills. Limitations exist with relying upon natural microbial populations for biodegradation of oil and chemically dispersed oil. The process of applying chemical dispersants to an oil spill introduces a new agent that could be the preferable target for microbial attack instead of the oil itself (NRC, 1989). In addition, the potential toxicological effects on these microbial populations from increasing the concentrations of chemical dispersants or dispersed oil in the water column are still unclear.

Another alternative that could be considered during an emergency response is the decision to not respond at all, meaning that the ICS could determine that the environmental tradeoffs for applying chemical dispersants would not provide net environmental benefit to the impacted area. In such a situation where net benefits or environmental tradeoffs are being evaluated, response teams must consider multiple aspects of the oil spill incident, including scale of spill, weather, mixing conditions, and proximity to sensitive natural resources, and weigh the option for allowing the slick to disperse naturally, without use of chemicals. The magnitude of the spill, mixing conditions, and properties of the spilled oil are perhaps the most influential parameters for this case. A relatively small oil spill that occurs in the surface waters of a marine environment which at the time has ideal mixing conditions from wind speeds no less than 7 – 10 knots or tidal currents ranging from 5 – 10 cm/s could possibly be dispersed naturally over a one
week period without any anthropogenic motivation (Lewis et al., 2010). Other natural processes that were previously mentioned, such as the type of oil spilled, water properties, and presence of microbes or other organisms with potential to uptake, process, and degrade oil particulates, could have an influence in inhibiting, accelerating, or even enhancing the natural dispersion of an oil spill. Whichever option is chosen for an oil spill response, one thing is for certain. There can be no inadequacy in the consideration of all influencing parameters of an oil spill incident, and no shortcuts taken in the route of response.
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CONFLICTS OF INTEREST

The author declares no conflict of interest that interferes with the objective scope of this research paper.
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