The Effects of Chemical Dispersants on Buoyant Oil Droplets

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Abstract

Chemical dispersants are designed to disperse and dissolve surface slicks of crude oil and diesel by lowering the interfacial tension between the slicks and seawater. The effects of sub-surface application of dispersant during deep ocean oil spills are not well understood; however, very large quantities of dispersants were applied at the broken wellhead, 1,500 m below the surface, during the 2010 Deepwater Horizon accident.

Following the Deepwater Horizon accident, laboratory experiments were conducted that have shown that smaller droplets are produced by the breakup of contaminant jets of oil discharging into seawater if sufficiently high concentrations (≥ 1%) of dispersants are mixed with the oil. These droplets subsequently form a buoyant contaminant plume that rises toward the surface. Small droplets may detrain from the plume due to ambient density stratification and currents and form subsurface intrusion layers. Droplet size is therefore an important factor in determining the fate of the oil.

No data exist on the effect of dispersants on the evolution of droplets in the contaminant plume during their buoyant rise through the oceanic water column. Toward this end, an experimental investigation was conducted. In this experiment, buoyant droplets of Oseberg Blend crude oil, similar to the oil released in the Deepwater Horizon spill, mixed with COREXIT 9500 dispersant at various concentrations, were suspended by a downward flow of synthetic seawater in a vertical water tunnel to simulate free-rise conditions. The droplets were monitored with video cameras over extended periods of time and the hydrocarbon components of the oil that were dispersed or dissolved in the seawater were analyzed with a GCMS.
The data indicate that the addition of dispersant to crude oil promotes reduction of droplet size during free-rise and that this evolution is strongly influence by the Dispersant to Oil Ratio (DOR). Video imaging revealed that droplet shrinkage occurs due to “tip streaming,” where larger droplets at sufficiently high DORs shed filaments of oil from their edges, or by tearing events. The extent and rate of shrinkage depends on DOR, with significant changes often occurring within the first 10-30 minutes of an experiment.

GCMS data were employed to attempt to quantify the phenomena observed in the video records. Seawater samples were extracted after 8 hours and dissolved and entrained hydrocarbons were collected using solid phase extraction. Integration of the chromatograms to estimate total hydrocarbon content, based on reference dilution GCMS injections of crude oil in hexane, indicate that the amount of oil dissolved and dispersed in water is very sensitive to DOR. Tests also demonstrate that most of the oil detected with the GCMS is entrained in the water phase as tiny droplets rather than being dissolved.

The results of this investigation suggest that droplets formed by the breakup of escaping oil jets during a undersea spill will shrink during their buoyant rise toward the surface if sufficient dispersant is mixed with the oil. The rate and extent of this reduction in droplet size depends strongly on DOR.
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1 Introduction

1.1 Chapter Outline

This chapter provides general information on chemical dispersants and their application to oil spills. Section 1.2 discusses the motivation for this exploratory experimental study. Section 1.3 presents a literature review of the effects of dispersants on crude oil. Section 1.4 provides an overview of this thesis and Section 1.5 summarizes the experimental approach.

1.2 Motivation for Study

Until recently, the petroleum industry has left difficult-to-access deep ocean oil reserves untapped. Due to increasing oil demand and prices, however, drilling deep water (i.e., $>\sim 1$ km depth) offshore wells has become more commonplace. Unfortunately, devising effective response strategies for spills from such wells is problematic, a point underscored by the 2010 Deepwater Horizon (DWH) incident and the three-month-long attempt to contain that spill.

The Deepwater Horizon was a semi-submersible ultradeep ocean drilling rig that sank while drilling an exploratory well in the Macondo Prospect in the Mississippi Canyon Block 252 in the Gulf of Mexico. Natural gas and mud expanded into the well riser and pushed upward to the rig where the gas ignited and exploded. The rig sank and eleven workers were killed. The blowout preventer, a fail-safe oil well sealing device, failed, and a large gusher of oil and gas spewed from the broken riser $1,500$ meters below the ocean surface. Numerous attempts to stop the spill were made until it was finally
sealed after 87 days by pumping cement through two relief wells. The Deepwater Horizon accident was the largest oil spill on water and third largest ever, exceeded only in quantity by the Gulf War Spill and the 1910 Lakeview Gusher.

During the DWH spill, chemical dispersants were applied for the first time under the ocean surface in an effort to reduce the environmental impact of the released oil. A combined total of 6.8 million liters (1.8 million gallons) of COREXIT 9500 and 9527 dispersants was estimated to have been used in an attempt to disperse and degrade an estimated 757 million liters (200 million gallons) of crude oil released from the broken well. Of these 6.8 million liters, nearly 3 million liters were applied by an ROV (remotely operated vehicle) directly to the leaking wellhead as shown in Figure 1.1.

Figure 1.1. ROV application of dispersants directly at the leaking wellhead during the DWH incident

The decision to apply dispersants underwater was made to try to reduce the amount of dangerous volatiles in the immediate vicinity of the surface oil slicks and to decrease the volume of dispersants required to treat these slicks (Lee, 2012). The
reduction of volatiles was an important safety concern to relief personnel working in the area. It was assumed that subsea application of dispersants would result in smaller oil droplets that would not reach the ocean surface. Surface-only application of dispersants would have required large quantities to disperse the slicks due to two factors. First, as oil weathers after contact with air and sunlight, a shell forms around the oil requiring more dispersant to penetrate and disperse the oil effectively. Second, a buoyant plume of oil and gas ascending from deep in the ocean, as in the case of the DWH spill, will diffuse horizontally as it rises and the contaminants will be spread over an enormous area of ocean when the plume surfaces. This will require more dispersant to cover the large slick at an effective dispersant-oil ratio (Lee, 2012).

While the decision to apply dispersants underwater was carefully considered prior to implementation, the actual effect of underwater dispersant application was unknown at the time (Committee on Understanding Oil Spill Dispersants, 2005) since previous dispersant research had focused primarily on the effectiveness of dispersants applied to surface slicks of oil.

A congressional report (Ramseur, 2010) on the DWH blowout estimates that up to 22% (167 million liters) of the oil that was released from the broken riser remains unaccounted for after taking into consideration human intervention (including oil recovered, burnt, skimmed, and dispersed) and natural processes (evaporation and dispersion). Figure 1.2 and Figure 1.3 shows charts included in that report. The error bars which can be seen in Figure 1.3 demonstrate the large uncertainty in the volume of dispersed oil.
Figure 1.2. Oil accounting pie chart (Ramseur, 2010)

Figure 1.3. Fate of oil released during DWH accident including uncertainty (Ramseur 2010).

There is evidence that the underwater application of dispersant may have contributed to this missing oil by promoting the formation of subsurface intrusion layers...
of fine oil droplets. Payne and Beegle-Krause (Payne & Beegle-Krause, 2012), while sampling the water column around the oil spill, observed a significant amount of oil in subsurface water, stating that: “oil sheens were frequently observed on the upper surface of [the sampled] standing water in Go-Flo bottles.” There was also evidence of undersea plumes of weathered oil in the vicinity of the original spills, confirmed by NOAA (Ramseur, 2010). Satellite images taken in the vicinity of the DWH spill before and during subsea dispersant application, presented respectively in Figure 1.4 and Figure 1.5, also showed extreme changes in the amount of oil reaching the surface.

Figure 1.4. Satellite image around DWH taken before application of subsurface dispersants
Based on the DWH experience, subsurface application of dispersants to deep ocean oil spills appears to have a profound impact on the distribution in the water column and ultimate fate of the released contaminants. The mechanisms behind the effects observed in the field remain poorly understood and warrant careful investigation under controlled conditions. Elucidation of these mechanisms would contribute to the refinement of predictive oil spill models and would significantly benefit the development of effective response strategies for future deep ocean oil spills.

1.3 Background and Previous Work

Chemical dispersants were developed to dissipate oil slicks from the ocean surface in order to reduce environmental damage to coastal habitats at the expense of ocean and seafloor habitats (Committee on Understanding Oil Spill Dispersants, 2005; Lunel, 1995). This is accomplished by lowering the interfacial tension between seawater and oil which, when provided energy from surface water waves, allows for the breakup of the slick into droplets. If the droplets are sufficiently small, then buoyancy becomes
negligible relative to ocean turbulence and Brownian motion and the droplets will be 
entrained by the motion of the water and submerge and disperse. A droplet less than 100 
μm in diameter is generally considered to be permanently dispersed (Ramseur, 2010; Li, 
et al., 2007). Over time, dispersed oil will be subject to dissolution, oxidation, microbial 
degradation, and deposition.

Chemical dispersants consist of three basic components: solvents, surfactants, and 
additives. The solvent acts as a carrier to transport surfactants and additives into the oil. 
Surfactants (surface acting agents) lower the interfacial tension between seawater and oil. 
Additives are used in small quantities to increase oil biodegradability, improve dispersant 
dissolution into oil slicks, or increase the dispersion stability (Clayton, et al., 1992).

During the Deepwater Horizon incident, both COREXIT 9500 and COREXIT 
9527 were applied to the spill. The surfactant component used in both dispersants is 
Dioctyl Sodium Sulfo succinate (DOSS) but the two formulations employ different 
solvents. COREXIT 9500 uses hydrotreated light petroleum distillates (Nalco, 2012) 
while COREXIT 9527 uses 2-Butoxyethanol (Nalco, 2012).

Surfactant molecules such as DOSS have both hydrophilic (polar) and lipophilic 
(non-polar) groups (Clayton, et al., 1992). The molecule acts as a bridge between the 
water (polar) and oil (non-polar) phases, altering the interfacial tension significantly. 
Interfacial tension, σ, is frequently interpreted as the energy needed to create a unit area 
of surface between two phase. Breaking waves provide this energy for surface oil slicks, 
while contaminant jets of oil and gas are the energy source at a broken wellhead. With a 
lower interfacial tension, the energy required to form droplets of a given radius (and 
associated surface-to-volume ratio) from a volume of oil in water will decrease.
The influence of $\sigma$ on the curvature of an interfacial surface can be seen from the Young-Laplace equation.

**Equation 1.1. Young-Laplace Equation:**

$$\Delta p = \sigma \left( \frac{1}{R_x} + \frac{1}{R_y} \right)$$

Here, $\Delta p$ is the capillary pressure difference between the two phases and $R_x$ and $R_y$ are the principal radii of curvature in two dimensions. The Young-Laplace equation is typically employed to discuss the shape of the meniscus of a liquid in a capillary tube. For a given value of interfacial tension, the capillary pressure must increase as the radius of curvature decreases. By extension to the case of droplets, the pressure differential between the ambient fluid and the fluid inside tiny droplets will be excessively high and unstable, unless the energy of the interfacial surface, i.e., the interfacial tension, is low.

A sufficiently small oil droplet, say, around 100 $\mu$m, will be entrained in the water column indefinitely when the droplet buoyant force becomes negligible with respect to natural water currents or Brownian motion. Smaller oil droplets will also weather more readily through photo-oxidation, bacterial digestion, and dissolution than large oil droplets because of their higher surface area to volume ratio (Clayton, et al., 1992). If, however, droplets become entrained in the deep ocean beneath the photic zone, then bacterial digestion will typically proceed slowly due to the limited amount of dissolved oxygen; anaerobic digestion of hydrocarbons is negligible in comparison to aerobic microbial digestion (Lee, 2012). This may in turn lead to a persistent cloud of very fine droplets.
Previous dispersant research has focused mainly on two areas – the efficacy of a given dispersant-crude oil combination on entraining oil, and methods to test and calculate the efficacy of dispersants.

Understanding the efficacy of specific combinations of crude oil and dispersant is necessary since the chemical composition of crude oils vary widely. As a result, a particular dispersant may or may not work well with different oils.

The efficacy of dispersants is based on their ability to remove surface oil slicks via droplet formation and entrainment. Various test methods have been proposed to quantify dispersant efficacy. These range from laboratory shaker table mixing tests such as the Swirling Flask Test (Clayton, et al., 1992), its slightly modified variant the Baffled Swirling Flask Test (Blondina, et al., 1999), or other similar small-scale mixing tests. In these tests, volumes of oil and some quantity of dispersant are added to synthetic seawater in a flask and then shaken for a pre-determined period of time before being allowed to stand for about 10 minutes to let a surface slick form. A sample of water and suspended oil is then extracted from below the surface slick and analyzed to determine the fraction of the oil that is dispersed in the seawater as tiny droplets. Larger-scale and more complicated methods such as experiments in wave tanks or model basins (Li, et al., 2007), and ocean trials (Lunel, 1995) have also been employed.

Previous laboratory shaker table experiments have shown that the application of dispersants to crude oil can reduce the size of droplets by an order of magnitude for the same mixing energy, promoting the formation of droplets with radii of 10s of microns instead of 100s of microns (Li & Garrett, 1998). If a similar reduction occurs when
dispersants are applied underwater near a broken wellhead, then, according to Stokes Law, the terminal velocities of those tiny oil droplets would decrease a hundred-fold.

\[
\nu_t = \frac{2(\rho_{\text{oil}} - \rho_{\text{seawater}})}{9\mu} g R^2
\]

Equation 1.2. Stokes Law

Droplet terminal velocity, \(\nu_t\), is proportional to the buoyant force due to density difference \(g(\rho_{\text{oil}} - \rho_{\text{seawater}})\), \(\mu\), the viscosity of the seawater, and \(R^2\), the square of the droplet radius. As terminal velocity decreases, droplets rising from deep in the ocean will take much longer to surface and will be subject to dispersive forces and dissolution.

Ocean testing has demonstrated that application of dispersants to a surface slick results in the dispersed oil being distributed into a larger volume of water (Lunel, 1995). Other experiments such as that of multi-phase buoyant plumes (Masutani & Adams, 2000; Tang, 2004; Socolofsky & Adams, 2000) and models of deep oil spills (Li & Garrett, 1998; Scolofsky, Adams, & Sherwood, 2011) have suggested that the size of the oil droplets can profoundly affect the transport, trajectories, and ultimate fate of the oil.

In 2005, the National Research Council (Committee on Understanding Oil Spill Dispersants, 2005) released a report on dispersants stating:

“In many instances where a dispersed plume may come into contact with sensitive water column or benthic organisms and populations, the current understanding of key processes and mechanisms is inadequate to confidently support a decision to apply dispersants”

This statement relates to surface application of dispersants near to shore. Subsurface application in deep water is even more complicated.
Model results and previous experiments of deep ocean oil spills indicate that droplet size is an important factor in the behavior of buoyant plumes. In the case of a subsea oil spill, the plume will generally comprise a mixture of very buoyant natural gas bubbles and less buoyant oil droplets that form when fluid instabilities break up jets of escaping oil.

Aside from a single field experiment conducted off the coast of Norway in 2000, information about the size of droplets formed from the breakup of jets of crude oil comes from the limited number of laboratory studies mentioned earlier. In the case of the Norway field test, 120,000 liters of crude oil and 10,000 standard cubic meters of LNG were released at a depth of 844 m (Rye, Cooper, & Johansen, 2003). The released oil and natural gas was tracked with echo sounders and the oil rise time as well as the resulting slick thickness was measured. The results were compared to the integral plume model (Johansen O., 2000) which predicted the surface time and location of the slick fairly well. No dispersants were employed in the field experiment. Using the data, other models were developed to simulate oil and gas behavior (Zheng, Yapa, & Chen, 2002).

Buoyant plumes of liquid and gas generally can be classified as being one of three types shown in Figure 1.6 (Socolofsky & Adams, 2000): 1) plumes that don’t detrain material until they surface; 2) plumes that exhibit distinct intrusion layers; and 3) plumes that continually detrain as they rise.
Detrainment occurs when the mixture of gas, oil, and seawater entrained from a lower depth that is denser than the local ambient seawater becomes neutrally or negatively buoyant as the plume rises. The heavy seawater component peels away from the main plume, drawing along with it very small droplets and bubbles. These tiny droplets and bubbles will form horizontal intrusion layers in the density stratified deep ocean environment. As a result, the size of oil droplets formed during deep ocean spills is an important factor in understanding the fate of the contaminant oil.

Following the DWH accident, a limited number of laboratory studies have been conducted to investigate how dispersants affect the size of droplets formed by the breakup of jets of crude oil issuing into seawater. Brandvik et al. (Brandvik, et al., 2013) performed jet breakup experiments in a large (40,000 Liter) non-pressurized tank measuring 3 m in diameter and 6 m tall. Oseberg Blend crude oil, a Macondo Well proxy oil, was injected into natural seawater through four different circular nozzles having diameters of 0.5, 1.5, 2.0, and 3.0 mm, at oil flow rates ranging from 0.2 to 5 L/min. COREXIT was pumped into the oil supply line at DORs of 0 to 1:25 at a location 1000 nozzle diameters upstream of the discharge point. The size of the droplets produced by

![Figure 1.6. Sketches showing characteristics of different plume types (Socolofsky and Adams 2000)](image-url)
the breakup of the oil jet was measured with a Fraunhofer diffraction optical particle sizer (Sequoia Scientific model LISST 100-X).

Applying the results of laboratory-scale jet breakup experiments to a full-scale deep ocean oil spill is problematic. Typical injector diameters employed in the laboratory do not exceed a few millimeters (Brandvik, et al., 2013; Masutani & Adams, 2000; Johansen, et al., 2013), while the broken riser in the DWH spill had a diameter of approximately 180 mm. Based on the recent results of Brandvik et al. (Brandvik, et al., 2013), Johansen et al. (Johansen, et al., 2013) have proposed a relationship for mean droplet diameter that utilizes a modified Weber number.

\[{\text{Equation 1.3. Weber Number Scaling Law}}\]

\[
\frac{d'}{D} = A * \text{We}^{-3/5}
\]

Here \(d'\) is the characteristic (e.g., volume mean; mass median) droplet diameter, \(D\) is the nozzle diameter, \(A\) is a proportionality factor and \(\text{We}\) is the Weber Number, defined as:

\[{\text{Equation 1.4. Weber Number}}\]

\[
\text{We} = \frac{\rho U^2 D}{\sigma}
\]

\(\rho\) is the density of the jet fluid, \(U\) is the velocity, and \(\sigma\) is the interfacial tension between the jet (i.e., oil) and ambient fluids (i.e., seawater). Johansen et al. (Johansen, et al., 2013) propose that the droplet size distribution can be estimated using the characteristic diameter calculated from Equation 1.3 by selecting an “appropriate” two-parameter distribution function, such as lognormal or Rosin-Rammler, and employing the laboratory data to identify a best-fit value of the second parameter which is assumed to apply regardless of the size of the jet.
While the above approach offers an attractive option to address the scale-up problem, validation of this model requires accurate data from larger scale experiments. Unfortunately, no such field test currently is planned.

1.4 Research Objective

While there have been many studies on the effectiveness of dispersants applied to oil slicks as well as on methods to test for effectiveness of dispersant and oil combinations, there has been little work performed to date on subsurface application of dispersants. The lack of knowledge about this subject has proven to be a problem when trying to determine the fate of oil released during the DWH spill - a point that was underscored by the large reported uncertainties.

Results of previous modeling and laboratory investigations suggest that droplet size may significantly affect the fate of oil released during deep ocean oil spills. Under certain conditions, small droplets form subsurface intrusion layers and may remain trapped or eventually surface at locations far from the spill site. This complicates spill response strategies and introduces uncertainties in assessing environmental impacts.

Dispersants reduce interfacial tension between oil and seawater which promotes the formation of droplets, provided that enough mixing energy is available from the fluid flow field. Dispersants were designed to dissipate surface oil slicks. During the DWH incident, dispersants were applied for the first time subsurface, at the broken wellhead. Recent laboratory experiments indicate that this mode of application can greatly reduce the size of droplets formed by the breakup of escaping oil jets (Brandvik, et al., 2013). Anecdotal evidence from the DWH spill suggests that a significant portion of the oil did not reach the surface and form a slick when dispersants were applied at the broken riser.
A model developed by Johansen et al. (Johansen, et al., 2013) based primarily on data from small-scale laboratory experiments, provides a means to estimate the distribution of droplet sizes produced by oil jet breakup in the presence of dispersants; however, it has not been confirmed that the results are valid for full-scale spills. Moreover, the distribution of droplet sizes may continue to evolve post-breakup in the buoyant plume.

If dispersants reduce the interfacial tension between oil droplets and the ambient seawater, then it is reasonable to expect that larger droplets that are initially generated from the jet may continue to break down into smaller droplets under the influence of hydrodynamic forces during their subsequent buoyant rise through the water column. Conversely, coalescence events can increase droplet size. It is unknown how dispersants influence these phenomena.

The objective of the present study is to investigate the effects of dispersants on the evolution of crude oil droplet size following jet breakup and during buoyant rise through the ocean water column. It is hypothesized that dispersants enhance the evolution of rising oil droplets; generally leading to a reduction in diameter over time, and that the proportion of dispersant mixed into the oil phase is a primary parameter that controls this evolution.

1.5 Research Approach and Organization

Experiments were conducted to determine the effects of DOR on buoyant oil droplets rising in seawater. The strategy adopted for this investigation was to observe a volume of dispersed oil in a simulated free-rise condition and to quantify the amount and species of hydrocarbons that transferred to the water phase.
Since it is impossible to observe the behavior of oil droplets ascending over more than a few tens of meters in a quiescent column of water in the laboratory, it was decided that rather than having the droplet move through water, water could be flowed over the droplet at a rate where the drag force balanced buoyancy. The droplet could then be held (nearly) stationary and observed for long periods of time, effectively moving from an Eulerian to a Lagrangian reference frame. This concept has been employed previously to study hydrate formation on gas bubbles (Maini & Bishnoi, 1981; Masutani & Adams, 2000). Parameters other than the DOR which are known to influence dispersant efficacy were held constant during an experiment. These parameters included oil-water ratio (OWR), temperature, salinity, and crude oil composition (Clayton, et al., 1992; Committee on Understanding Oil Spill Dispersants, 2005). Some of the parameters were changed in different tests.

Video cameras were employed to monitor and record droplet behavior. Water samples were collected and analyzed to determine relative amounts of dispersed and dissolved oil.

Chapter 2 provides details of the experimental facilities. Experimental procedures are described in Chapter 3. The results of the experiments are presented in Chapter 4, and Chapter 5 provides a summary of the results and the conclusions of this study as well as suggestions for future work.
2 Experimental Setup

2.1 Chapter Outline

This chapter describes the experimental facility employed in this study. Section 2.2 provides an overview of the system. Details of the flow apparatus are discussed in Section 2.3. Section 2.4 reviews the equipment used for water sampling and hydrocarbon analysis.

2.2 System Overview

Buoyant oil droplets were suspended in a recirculating, downward flowing, vertical water tunnel. To allow the suspension of a collection of different sized droplets, the tunnel included a diffuser section, which created a velocity gradient in the flow direction to match their different terminal velocities.

The flow apparatus consisted of six main components: a water tank, a water tunnel, a variable speed gear pump, a temperature control system, an oil injection system, and various sensors. These are described in greater detail in Section 2.3. Figure 2.1 presents a photograph of the flow apparatus.
At the end of an experiment, the seawater was tested for dispersed or dissolved hydrocarbons. A facility was designed to extract hydrocarbons from a sample of the recirculated seawater utilizing a reverse-phase solid phase extraction (SPE) method. The SPE methodology was selected due to its ability to highly concentrate hydrocarbons for analysis with minimal usage of chemicals compared to other methods such as liquid-liquid extractions.

The sample extraction system consisted of a vacuum manifold, vacuum pump, vacuum gauge, needle valve, and an SPE frit used for concentrating hydrocarbons.
Figure 2.2 shows a diagram of this system. A volume of seawater from the water tunnel flow loop, typically between 1-2 liters, was drawn through a SPE frit with the vacuum pump. Hydrocarbons in the seawater bonded to the frit packing material via Van der Waals interactions. The deposited hydrocarbons were washed off of the silica packing with a small volume of hexane. The solution was then injected into a GCMS for analysis. Section 2.4 discusses the extraction and analysis components in detail.

![Flow diagram of the SPE system](image)

Figure 2.2. Flow diagram of the SPE system

### 2.3 Flow Apparatus Components

A schematic diagram of the flow apparatus is provided in Figure 2.3.
The flow apparatus consisted of six main components: a water tank, a water

tunnel, a variable speed gear pump, a temperature control system, an oil injection system,

and sensors. The water tunnel was completely submerged in the cylindrical water tank

and sealed against the base of the tank. A gear pump drew seawater from ports in the

bottom of the tunnel, inducing a downward flow. The seawater flowed through a series

of sensors and temperature control elements before being reintroduced at the top of the

water tank. Two thermistors, located immediately upstream of the water tank and

downstream of the water tunnel, were used to monitor seawater temperatures. An inline

flowmeter was used to record flow rates. The temperature of the seawater was controlled

using a heat exchanger and constant temperature bath. Data from the two thermistors and
the flowmeter were data logged using two DAQ (data acquisition) boards and LabView software. Oil or oil-dispersant mixtures were manually injected into the bottom of the water tunnel through PEEK tubing attached to a syringe.

**Water Tank and Base**

Figure 2.4 shows a photograph of the bottom of the water tank, as well as the oil injection system.

![Figure 2.4. A photograph showing the water tank, tank base, and oil injector.](image)

The water tank consisted of a 6 ft. (1.8 m) tall, 6 in. (152 mm) OD, 0.25 in (6.35 mm) wall, clear, cast acrylic tube. A flange was fabricated from a cast acrylic plate and was cemented to the base of the tube. This base plate was drilled and tapped with four
3/8” (10mm) seawater removal ports which were positioned around an oil injection port located on the tube centerline. The tubes used to remove seawater were connected together in a 4-into-2-into-1 configuration. The tubes were cut to equal lengths to minimize head loss differences between the ports, to prevent flow distribution irregularities.

**Oil Injection**

To inject oil into the flow in the water tunnel, a length of 1/16” OD (1.60 mm) x 0.040” ID (1.01 mm) PEEK tubing was threaded through a 0.25 in. (6.35 mm) OD stainless steel tube connected to a fitting installed in the port in the center of the water tunnel base. A 3 ml polypropylene syringe was attached to the end of the PEEK tubing and was used to manually inject oil into the water tunnel. Figure 2.4 shows the oil injection system attached to the water tank and base.

**Water Tunnel**

The water tunnel was used to suspend oil droplets by balancing the buoyancy force with a flow-induced drag force. One of the design objectives of the water tunnel was to provide a steady and relatively uniform velocity field with low turbulence levels, since this would minimize the disruptive forces acting on the droplets. In an actual oil spill plume, rising droplets would be subject to ocean currents and turbulence, and wake flow induced by neighboring droplets and bubbles.

Synthetic seawater was circulated downward through the water tunnel with a gear pump. In the water tunnel, the seawater flows, in sequence, through a long radius nozzle, a cylindrical viewing section, a diverging conical section, and finally through the base and out of the water tank. Seawater removed from the base of the tunnel flows through
the temperature control system and sensors before being discharged through a tube positioned above the free surface of the water at the top of the tank.

An ISA long radius nozzle, machined from acrylic, was used to accelerate the flow into the constant cross sectional area viewing section and reduce turbulence intensity. Figure 2.5 displays a photograph of the nozzle used. Figure 2.6 shows the dimensions.

![A photograph of the custom machined ISA long radius nozzle.](image)

*Figure 2.5. A photograph of the custom machined ISA long radius nozzle.*
Figure 2.6. Dimensions of the ISA long radius nozzle used shown in terms of “D” and “d” – the inlet and outlet diameters, respectively.

The clear viewing section of the water tunnel was made from a 4 in. (102 mm) length of 1.5 in. (38 mm) O.D. x 1.0 in. (25.4 mm) I.D. cast acrylic tube. A slightly modified inverted Imhoff settling cone attached to the exit of the viewing section was employed as a conical diffuser. The Imhoff cone’s half angle is less than 7.5°, which is believed to be small enough to avoid flow separation (Sparrow, Abraham, & Minkowycz, 2009). Streamwise velocity in the diffuser decreases rapidly, by a factor of about 20, as the flow proceeds downward from inlet to outlet. This wide range of velocities allowed various sizes of droplets to be suspended for observation. This was essential for experimental cases in which higher concentrations of dispersants were used. During these tests, droplet sizes changed drastically over a few minutes, resulting in a wide range of terminal velocities. At the velocities used to suspend oil droplets in the 1” viewing
section, the velocity at cone exit would be roughly 0.007 m/s, or roughly a 300 micron diameter droplet.

The velocity field within the cylindrical viewing section was mapped with a Laser Doppler Velocimeter (LDV) for various flow rates. These measurements are described in Chapter 3 and the results are reported in Chapter 4.

**Pump, Motor, and Speed Controller**

A Micropump Series 2200 cavity gear pump, which has a maximum flow rate of 12 l/min, was used to circulate the synthetic seawater through the facility. The pump was magnetically coupled to a 1-HP Leeson 3-phase AC motor (Model # C6T34FK1C). Motor speed could be programmed with a Leeson Speedmaster Adjustable AC Motor Controller (Model # 174931), which is capable of controlling the frequency with a resolution of 0.01 Hz.

**Temperature Control System**

A stainless steel counter-flowing 10-plate heat exchanger from Bell and Gossett (Model BP 400-010) was coupled with a VWR Model 1156D heating/cooling circulating bath and used to control the temperature of the synthetic seawater flowing through the water tunnel. This heat exchanger and chiller/heater bath combination was able to hold the seawater temperature steady at a selected value between 5°C and 50°C. Temperatures outside of this range were not tested.

**Sensors**

Two thermistor probes (Omega Engineering Model # TJ36-44004-1/8-12) were used to monitor the temperature of the synthetic seawater circulating through the system. The probes were installed in the flow lines at the entrance and the exit of the water tank.
Thermistors operate by relating a change in electrical resistance to temperature change. Temperatures can be approximated by the third-order Steinhart-Hart Equation approximation, shown below, over a given temperature range.

\[
\frac{1}{T} = a + b \ln(R) + c \ln(R)^3,
\]


Where \( T \) is the temperature, \( R \) is the electrical resistance of the thermistor, and \( a \), \( b \), and \( c \) are constants determined empirically. The Steinhart-Hart coefficients for the thermistors were provided by the manufacturer. The thermistors were accurate to 1% within 0°C to 100°C.

A Great Plains Industry (GPI) ½ inch FNPT Industrial Grade 1-10 GPM (gallon per minute) turbine-type water flowmeter was used to monitor seawater flow rates. Fluid passing through the meter rotates a turbine, which generates an electric signal at a pickup coil. This signal is related to the flow rate through a k-factor determined by the manufacturer. An optional Pulse Output Module was employed to provide a square wave signal to a DAQ board. The flowmeter was tested to have an accuracy of +/- 2% of the reading. Figure 2.7 and Figure 2.8 presents an image of the flowmeter and thermistors integrated into the flow apparatus.
Figure 2.7. A photograph displaying the flowmeter and thermistor on the inlet pipe.

Figure 2.8. A photograph of the thermistor attached to the water tank outlet.
Two DAQ boards were utilized in these experiments. The counter input of a Cole-Parmer 18200-00 DAQ board was employed to obtain data from the flowmeter pulse output module. The two thermistors were connected to a Cole-Parmer 18200-30 DAQ board, with a four-wire configuration. Both DAQ boards were connected via USB cables to a computer and LabView software was used to interpret, display, and datalog the sensor measurements. Figure 2.9 shows the LabView front panel used for monitoring and datalogging the experiment.

![LabView front panel](image)

*Figure 2.9. An image of the LabView front panel used during datalogging and monitoring of temperatures and flowrates*

### 2.4 Hydrocarbon Analysis Components

**Solid Phase Extraction**

Two different methods are used in solid phase extraction (SPE): normal phase or reverse phase extraction (Discovery Sciences, 2012). Normal phase extraction uses a packing material which has been modified to have polar elements. It is used to extract
polar analytes from a non-polar solvent or to filter out polar molecules from a non-polar analyte.

The reverse phase extraction method, as the name suggests, works in reverse and uses packing materials modified to have non-polar elements. For this experiment, a reverse phase extraction method was employed for the collection of non-polar analytes from polar solvents, i.e., hydrocarbons from seawater. The SPE methodology has the advantage of being able to extract an analyte from a large volume without using as much solvent as liquid-liquid extraction methods.

In this investigation, a 4 ml reverse phase solid phase extraction high flow C-18 frit from Grace Scientific was utilized. The packing material was contained in a 4 ml open-top cartridge with a slip fit Luer base. The packing material consisted of a porous bed of octadecyl (C-18) bonded, end-capped silica (Sigma-Aldridge, 1998). Figure 2.10 is a photograph of the C-18 High Flow frit. Figure 2.11 shows the chemical reaction used to bond C-18 molecules to the porous silica packing material.

*Figure 2.10. Photograph of an SPE frit.*
Chemical reaction used to endcap the silica substrate with the C18 molecule.

As a polar solvent (e.g., seawater) containing non-polar molecules (e.g., hydrocarbons) passes through the silica bed, the C-18 molecule attached to the ends of the silica bed attracts and bonds to non-polar molecules via Van der Waal forces. After extraction, the non-polar molecules can be washed off of the packing material using a small volume of hexane, or some other strong, non-polar solvent.

Vacuum Manifold

A Vaccubrand 2C diaphragm-type pump was used to draw seawater through the frit. The pump created a slight vacuum in a manifold to which the SPE frit was attached. The vacuum was monitored with a liquid filled, bourdon tube, differential pressure gauge, and adjusted manually with a needle valve. The required vacuum was determined through trial-and-error to achieve a seawater flow rate of about 10 ml/minute. Extraction times varied from test to test by up to 60 minutes for a nominal 2 liter seawater sample, depending on the amount of hydrocarbons in the water. A higher concentration of hydrocarbons in the water would result in heavy deposits on the frit which would restrict the flow of seawater through the frit, significantly increasing extraction time.

Gas-Chromatography/Mass-Spectrometry

Gas chromatography-mass spectrometry (GCMS), utilizes two separate instruments, a gas chromatograph and a mass spectrometer, working in conjunction. A GCMS is better able to identify a specific molecule, than either instrument alone. The
gas chromatograph section of the GCMS separates a vaporized mixture of molecules into individual components by means of a capillary column, typically designed for specific classes of substances. The time that it takes molecules of different substances to pass through the column, known as the retention or elution time, varies as a result of their affinities to the column materials. Different molecules that have similar elution times through a particular column typically cannot be identified unambiguously with a simple GC. The mass spectrometer section, however, provides a means to do this. Molecules leaving the GC enter the MS where they are dissociated into ionic fragments and the mass-to-charge ratios of these fragments are determined. This information is used to identify the most likely compound(s). The relative quantity of the compound in the sample can also be determined.

A Scion Bruker 400-GC Series GCMS was used to analyze the hydrocarbons extracted from the seawater by SPE. The analyze hydrocarbons suspended in hexane solvent were injected into the GCMS. The sample was vaporized in the GCMS oven and the vapor was carried through the capillary column with Helium gas. A stock photograph for the GCMS used is shown in Figure 2.12.
Figure 2.12. A stock photograph of the Bruker Scion series GCMS.
3 Experimental Methods

3.1 Chapter Outline

This chapter reports the experimental methods and procedures employed in the present investigation. Section 3.2 discusses the calibration procedures for the sensors installed in the flow system. Section 3.3 describes the methods used to characterize the oil. Laser Doppler Velocimetry measurements to determine the flow field of the water tunnel and the test protocol followed in the oil droplet evolution experiments are covered in Sections 3.4 and 3.5, respectively. Finally, Section 3.6 discusses the procedures used to sample and analyze the seawater.

3.2 Sensor Calibration

Three sensors were used to monitor conditions in the water tunnel during the droplet experiments: a flowmeter and two thermistors. The methods used to calibrate these sensors are described below.

**Flowmeter Calibration:**

Fluid passing through the inline flowmeter rotates a turbine which induces electric currents (pulses) in a pickup coil. The flowmeter is calibrated at the factory using fresh water at 21°C to determine the value of the (constant) K-factor, which is the number of pulses per gallon of liquid. The accuracy of the meter specified by the manufacturer is ±2% of reading (Great Plains Industries, Inc., 2004). A catch and weigh test confirmed that the flowmeter was accurate to within 2% of readings.

**Thermistor Calibration**

The Steinhart-Hart coefficients for the two thermistor probes were provided by the manufacturer. According to the manufacturer, the accuracy of the thermistors were
±0.2°C at 25°C with a maximum temperature of 150°C (Omega Engineering, Inc., 2012). Prior to assembly of the flow system, the thermistor temperature measurements recorded by the LabView program were compared against an ice bath and boiling water bath and found to be within 1% of readings.

### 3.3 Oil Characterization

The physical properties of the crude oil influence hydrodynamic break up and mass transfer. Toward this end, measurements were performed to determine interfacial tension, viscosity, and density of the crude oil samples used in this investigation. The methods and instrument employed are outlined below, and results are presented in Chapter 4.

**Tensiometer Calibration and Measurement:**

Interfacial tension, traditionally given in units of dynes/cm (1 dyne = 10^{-5} N), is probably the most important factor affecting droplet formation. A DuNouy dual-direction ring tensiometer was used to determine the interfacial tension between seawater and oil, at differing DOR concentrations.

A DuNouy tensiometer measures the force required to move a platinum-iridium ring from one fluid to another. Figure 3.1 is a photograph of the device. Interfacial tension was calculated from the following equation:

\[ \vec{P} = \frac{F}{2L} \]

*Equation 3.1. Interfacial Tension Equation.*

where \( \vec{P} \) is the interfacial tension, \( F \), is the measured force in dynes, and \( L \) is the ring circumference. 2\( L \) is an approximation of the total wetted perimeter of the ring with interfacial tension forces acting on both the inner and outer circumference of the ring.
Figure 3.1. Photo of the DuNuoy tensiometer used for interfacial tension measurements.

Tensiometer ring motion was constrained to move perpendicular to the fluid to ensure that the measured force was normal to the interface. The force on the ring due to interfacial tension is balanced by a torsion spring attached to a Vernier dial. Essentially, the tensiometer is a highly sensitive and accurate spring scale; however, instead of force, the scale is calibrated to measure in dynes per cm – the force per length of a platinum ring with known circumference.

To calibrate the tensiometer, a known mass was placed on the platinum-iridium ring. The weight of the mass was taken as the value of $F$ in the previous equation, and the corresponding value of $\vec{P}$ for the known ring circumference was calculated. If the Vernier dial readout did not match this value of $\vec{P}$, then moment arm and counterweight
adjustments were made, and the process was repeated until the proper value of $\vec{P}$ was displayed.

The procedure to perform interfacial tension measurements comprised the following steps: first, the tensiometer table was leveled using three adjustable-height screws on the base of the instrument. Next, a wide shallow dish was placed on the table. A solution of Instant Ocean Aquarium Mix and particle and carbon filtered tap water at 35 ppt salinity was prepared. Synthetic seawater, the denser fluid, was poured into the dish first. The ring was then immersed into the seawater by raising the table. A well-mixed volume of oil and dispersant at a selected DOR was poured over the water into the dish. The table was then lowered slowly while monitoring the Vernier dial. As the ring reached the fluid interface, the interfacial tension acting on the ring resisted the motion, and the indicator shifted from zero. The Vernier dial was then adjusted to return it to zero. These incremental adjustments continued until the ring broke free of the interface. The reading on the Vernier dial at this breaking point was the interfacial tension. To verify the accuracy of the tensiometer, the interfacial tension between DI (deionized) water and air was measured and checked against the value in the literature (72.8 dynes/cm) periodically.

Between measurements, the platinum-iridium ring was rinsed with hexane, allowed to dry, and then passed through the yellow oxidizing section of a flame as specified by the manufacturer (CSC Scientific Company, Inc.). While the manufacturer stated that the accuracy of the tensiometer was ±0.1 dyne/cm, it was found that, in practice, the repeatability was closer to ±0.5 dyne/cm. Interfacial tension below 1
dyne/cm could not be accurately determined. The results for the oils used in this investigation are reported in Chapter 4.

**Viscometer Calibration and Measurement:**

A SVM 3000 Stabinger viscometer was used to characterize the viscosity and density of the oil and oil/dispersant mixtures at various temperatures. The viscometer is equipped with a Peltier (thermoelectric) element to control the temperature of the fluid being measured. Figure 3.2 is a photograph of the instrument.

![Figure 3.2. Stock photo of a SVM 3000 viscometer.](image)

The Stabinger viscometer operates on the basis of torque transfer depending on fluid viscosity. The viscometer measures dynamic viscosity in the range of 0.2 to 10,000 mPa-s, kinematic viscosity measurements from 0.2 to 10,000 mm²/s, and density measurements from 0.65 to 2 g/cm³, with accuracies of 0.35% of measured value for viscosities, and 0.0005 g/cm³ for density measurements (Anton Paar, 2002).
The fluid being characterized was injected into a hollow cylinder containing a free floating rotor. The center rotor contains a magnet which induces eddy currents in surrounding wires when rotated. The hollow cylinder was rotated at constant speed, and due to the viscosity of the injected sample, the center rotor also rotated. The eddy currents induced by the center rotor act as a brake on the rotor. The eddy current also is used to determine the speed of the rotor. When the rotor reaches steady-state, the eddy current braking torque is in equilibrium with the torque acting on the rotor as a result of fluid viscosity. This force balance is used to calculate the dynamic viscosity of the injected sample.

Density was measured with an oscillating U-tube mechanism in-line with the viscosity cell, allowing for simultaneous measurements. To determine sample density, a glass U-tube was filled with the fluid and oscillated. The density of the fluid affects the resonant frequency of the tube which is modeled as a simple mass-spring system. The resonant oscillation frequency, \( \tau \), was measured and converted directly to density, \( \rho \) with the following equation.

\[
\text{Equation 3.2. Equation for density measurements using a glass U-tube} \\
\rho = \tau^2 A - B
\]

The constants A and B are determined by performing measurements of two samples of fluids with known densities beforehand.

Kinematic viscosity is calculated using values of the measured dynamic viscosity and density of the fluid.

The procedure followed to measure the viscosity of a sample was as follows: a well-mixed volume of crude oil and COREXIT dispersant at a selected DOR was drawn into a 6 ml syringe which was then connected to the viscometer. 2 ml of the fluid was
injected into the viscometer initially and allowed to circulate for 15 seconds. An additional 1 ml of fluid was then injected to purge any gas bubbles and the viscosity was measured. The viscometer was programmed to test density and viscosity of the sample from 20°C to 40°C in 10°C increments. Between samples, the viscometer was flushed with hexane and dried with air. The results are reported in Chapter 4.

3.4 Water Tunnel Flow Profile Determination

The desired velocity field in the observation section of the water tunnel would be uniform over most of the flow area with small boundary layers and low turbulence. This would minimize movement of the droplets and would represent a relatively quiescent environment compared to conditions in the actual plume where droplets are subjected to wake flows (from preceding droplets and bubbles), currents, and higher turbulence. Considerable trial-and-error modifications were made to the water tunnel during shakedown testing of the facility to obtain what was believed to be an acceptable flow field. Thereafter, measurements of the stream wise velocity component (U) were performed in the straight observation section for four different flow rates. These measurements are described below.

Velocity measurements were performed using the Laser Doppler Velocimeter (LDV) portion of an Aerometrics Phase Doppler Particle Analyzer. Laser Doppler Velocimetry is a non-intrusive, optical measuring method. This technique calculates the velocity of particles advected by a fluid by measuring the Doppler shift of refracted light from those particles.

Dark and light bands of light, called fringes, were created by intersecting two collimated (well aligned) and coherent (same phase) laser beams of the same wavelength.
The two beams were obtained by splitting a single beam, which ensured both coherence and wavelength. The power in both beams was adjusted to be identical prior to LDV measurements. The width and spacing of the fringe was dependent on the angle of intersection and laser wavelength. As a particle passed through the fringe, light from the bright bands was refracted and reflected by the particle while being Doppler-shifted due to the particle’s velocity. The refracted light was then captured by a receiver focused on the beam intersection volume. The Doppler-shift observed was used to calculate the particle velocity.

The output beam from a water cooled 1W Lexel Model 85 Argon-ion laser was split into two parallel-polarized, equal-intensity beams using a Bragg cell which also eliminates the directional ambiguity of the measurement. The beams were collimated, and then focused to intersect each other with a 250 mm focal length lens. Optical interference of the two beams at their intersection creates a series of equally spaced light and dark fringes that move in one direction at a constant rate due to the Bragg cell. The beams were oriented such that they emerged from the focusing lens at 6 and 12 o’clock positions, so that the fringes were perpendicular to the streamwise (vertical) flow coordinate, which allowed measurements to be made of that velocity component.

Small particles (e.g., solids, bubbles, droplets) moving with the fluid that pass through the fringes scatter light that is captured by an optical receiver unit fitted with a 300 mm focal length lens. The receiver is positioned 50° off-axis (where 0° is in the direction of propagation of the laser beams) in a forward-scatter configuration. While most forward-scatter LDV measurements are conducted around 30° off-axis due to the relatively high scattering intensity at this angle, 50° was selected for these tests to allow
measurement of velocities near the observation section walls. Due to the design of the water tunnel, a receiver angle of 30° would result in the back tunnel wall being near to or directly between the measurement volume and the receiver. The laser beams would illuminate the acrylic wall cylinder as they passed through the tunnel and would overwhelm the scattering signal from the measurement volume.

Scattered light collected by the receiver lens passes through a 150 μm slit which reduces the measurement volume before being transmitted by a fiber optic cable to the photodetector and data processing unit. The optical sample volume was calculated to be about 0.0034 mm³. Based on the known fringe spacing and the frequency of the Doppler modulation of the scattered light, the streamwise velocity can be calculated.

Alignment

The LDV system was aligned prior to each test. The Bragg cell and other optical components were adjusted to maximize and to balance the intensity of the two beams produced by the Bragg cell to within 0.5 mW. The absolute power output of the beams would vary day-to-day by up to 2 mW.

The water tunnel was filled with tap water that was filtered with an activated carbon filter and a 5 μm particulate filter before being seeded with 3-5 μm diameter, hollow glass beads with specific gravities of 1.05-1.15. Approximately 0.1 to 0.25 g of beads were added to 30 liters of water. A seed particle with a density nearly equal to that of water was selected to ensure that buoyant forces were negligible. The water tunnel was mounted on a two-dimensional (horizontal-vertical) translation stage and moved relative to the fixed optical sample volume. Streamwise velocity at five radial points along the diameter of the cylindrical observation section, on one side of the centerline,
approximately 75 mm downstream of the exit of the contraction, was measured at four
different flow rates. Triplicate measurements were performed at each location. Results
are reported in Chapter 4.

Table 3.1 summarizes the conditions employed during the LDV measurements of
streamwise velocities in the water tunnel.

*Table 3.1. User Selected Parameters for LDV setup*

<table>
<thead>
<tr>
<th>Seed Particles</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow Glass Spheres</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>1.05 to 1.15</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>1.5</td>
</tr>
<tr>
<td>Size</td>
<td>3 to 5 µm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LDV Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmitter Focal Length</td>
<td>250 mm</td>
</tr>
<tr>
<td>Slit Width</td>
<td>150 µm</td>
</tr>
<tr>
<td>Particle Size Range</td>
<td>0.5 to 85 µm</td>
</tr>
<tr>
<td>Particle Velocity Range</td>
<td>-73 to 73 m/s</td>
</tr>
<tr>
<td>Receiver Angle</td>
<td>50 degrees</td>
</tr>
<tr>
<td>Slope</td>
<td>0.653</td>
</tr>
<tr>
<td>Receiver Focal Length</td>
<td>300 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Probe Volume</td>
<td>0.0034 mm³</td>
</tr>
</tbody>
</table>

3.5 Droplet Experiment Protocol

This section describes the methods employed to prepare the synthetic seawater
and the mixtures of crude oil and dispersant, as well as the procedure to inject the oil
sample into the water tunnel, and the protocol used to stabilize the droplet in the
observation section.
Seawater Preparation

Synthetic seawater was employed in all droplet experiments. Although natural seawater was available, chemical composition and biological content varies depending on the collection location.

A previous study (Blondina, et al., 1999) found that salinity can greatly influence the effectiveness of dispersants on oil (specifically, COREXIT 9500 and 9527 which were used during the DWH accident). Therefore, the salinity of the seawater was carefully controlled in the present investigation. Instant Ocean, an aquarium salt mixture manufactured by Aquarium Systems and which has been employed in a number of earlier dispersant studies, was used to synthesize seawater. While natural seawater salinity can vary from 31 to 38 ppt (parts per thousand, by weight), a salinity of 35 ppt was selected for this study. This value was chosen since the salinity of 90% of water in the oceans fall within 1.1% of 34.7 ppt (Pilson, 1998).

Synthetic seawater prepared with Instant Ocean closely resembles natural seawater except it has a higher buffer content and lower organic components (Hovanec, 2008). Instant Ocean mix was dissolved in tap water that was filtered through a 5 µm activated carbon-impregnated cellulose filter. A conductivity meter was used to check the salinity. The water was then circulated through the water tunnel for about 30 minutes to fully dissolve the salt. The salinity was then rechecked and adjusted to attain 35 ppt. Finally, the synthetic seawater was circulated through the tunnel for 12-14 hours to fully mix and aerate before the start of the experiment.
Oil-Dispersant Mixture Preparation

Brandvik et al. (Brandvik, et al., 2013) reported that oil jet breakup is profoundly affected at DORs of 1:25 or less. The range of DORs examined in the present study was \( \leq 1:50 \). Preparation of samples therefore required mixing very small volumes of dispersant with crude oil. Accurately pipetting small volumes of the dispersant proved to be difficult due to its viscosity. Instead, the known dispersant density was used to calculate the mass of the desired volume, which was then weighed with a balance and mixed with the oil. The crude oil and dispersant-oil mixtures tended to settle and separate fairly quickly. To homogenize the samples, a magnetic stirrer plate was used at the highest setting for 30 minutes immediately prior to injection.

Oil Injection

During the water tunnel experiments the seawater flow rate was initially set to a nominal value which had been determined by trial and error to keep the oil from being flushed from the tunnel or escape through the contraction. 2 ml of the homogenized sample was drawn into a polypropylene syringe. About 1 ml of the sample then was slowly injected to fill the empty injection line, which had a volume of \( \sim 0.75 \) ml. Once a small volume of sample emerged from the line indicating that it had been filled, 1 ml of the sample was then injected into the tunnel. The rate of injection varied with DOR. Higher DOR tended to immediately break up into a fine cloud of droplets if injected too rapidly, while pure crude oil would form one or two large droplets at the injector. The droplets were allowed to rise through the Imhoff cone and the seawater flowrate was adjusted as necessary to stabilize droplets in the observation section.
Oil Droplet Balancing and Monitoring

Seawater flow rates varied between tests. Samples with higher concentrations of dispersants (i.e., lower DORs) required much lower flow rates due to the smaller initial droplets which have lower terminal velocities. The initial flow rates for different DORs were determined through trial and error before an experiment and are reported in Chapter 4. During a test, seawater flow rates were also adjusted depending on droplet behavior, to balance changes in terminal velocity.

The oil droplets were monitored with video cameras for over 8 hours. The first hour was the most critical, with most droplet size evolution occurring in the first 15 minutes after injection for the higher DOR tests. After 8 hours of circulation, 2 liters of seawater were sampled for GCMS analysis.

Tank and Tunnel Cleaning

To avoid contamination between experiments, the water tank and tunnel were disassembled and washed thoroughly with Dawn dishwashing detergent (which is very effective in removing oil deposits) after each test. The remainder of the flow system, including tubing, pumps, and sensors, which could not be scrubbed was triple flushed with soapy water, before being flushed with particle- and carbon- filtered tap water. The water tank was also triple flushed with particle- and carbon-filtered tap water before being filled with seawater. The oil injection line was triple flushed with hexanes followed with filtered tap water to remove oil and dispersant residue.
3.6 Water Analysis Protocol

Hydrocarbon Extraction Protocol

Immediately after a test, a fixed volume (typically 2000 ml, but for one case, 4000 ml) of the seawater that had been continuously circulated through the water tunnel was diverted into a beaker through a tee fitting in the flow line while the pump continued to operate, ensuring a representative sample of the water. 2000 ml of the seawater was drawn through a C-18 reverse phase solid phase extraction frit with a vacuum pump to collect the dissolved and finely dispersed hydrocarbon components. The frit was first conditioned by passing 5 ml of methanol, followed by 5 ml of deionized water per the manufacturer’s instructions. This conditioning step activates the C-18 molecules (Discovery Sciences, 2012). A typical 2000 ml sample required about 4-5 hours to pass through the frit. After extraction, the frit was rinsed with 10 ml of deionized water and stored in a freezer before GCMS analysis. The freezer was used to prevent devolatilization of hydrocarbons from the frit.

GCMS Analysis Protocol

Hydrocarbons deposited on the C-18 frits were washed off with 1 ml HPLC grade hexane. This resulted in a 2000X concentration; i.e., the hydrocarbons contained in 2000 ml of seawater were concentrated into 1 ml of hexane. This solution was then injected with an auto-sampler into the Bruker Series 400-GC GCMS for analysis.

Hexane was selected as the solvent of choice because it is known from previous experience to have good replicability when used in GCMS injections. Hexane also was the strongest non-polar solvent compatible with the C-18 SPE frits used in these tests (Discovery Sciences, 2012). Since slight GCMS signal variations in identical samples
between runs were observed during shakedown tests, a known concentration of toluene (100 ppmV) was added to the hexane used during frit washing to calibrate the chromatograms.

To determine the fractions of hydrocarbons collected on the frits that were dissolved in the seawater versus dispersed as very fine droplets, another experiment was conducted in which a 4000 ml volume of seawater was sampled 8 hours after injecting a 1:50 DOR sample into the circulating water tunnel. Half of this seawater sample was passed through a Whatman GF/C filter before being drawn through a frit, while the remainder was drawn through a second frit unfiltered. The Whatman GF/C filter removes dispersed oil particles larger than about 1.2 μm (Sigma-Aldrich, 2014) while allowing all the dissolved hydrocarbons (and any smaller droplets) to be collected by the frit. The results are summarized and reported in Chapter 4.
4 Experimental Results and Discussions

4.1 Chapter Outline

This chapter presents the results of the water tunnel experiments as well as the oil characterization and LDV data. Section 4.2 provides information on important experimental parameters, specifically, oil property data and the velocity profile in the water tunnel observation section. Representative images of droplet behavior extracted from the video data and the results of GCMS analyses of the water samples are reported in Section 4.3.

4.2 Experimental Parameters

Oil Properties

A Norwegian crude oil, Oseberg Blend, was used in these experiments. It is a low viscosity, light paraffinic blended oil similar in composition to the Macondo well crude oil that was released during the DWH incident. Oseberg Blend also was employed in the recent jet breakup investigation of Brandvik et al. (2013). Both COREXIT 9500 and 9527 dispersant were applied to the DWH spill; however, COREXIT 9500 was used in 88% of the dispersant applications (NOAA, 2012) and was therefore selected for the present study.

Table 4.1 provides information on Oseberg Blend. Manufacturer’s data on COREXIT 9500 are given in Tables 4.2 and 4.3.

Following the procedures described in Chapter 3, the interfacial tension, kinetic and dynamic viscosities, and the density of the oil at different values of DOR were determined and are reported below.
Table 4.1. *Oseberg Blend crude oil properties* (Resby & Wang, 2004)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>0.8393</td>
</tr>
<tr>
<td>Pour Point</td>
<td>-24 °C</td>
</tr>
<tr>
<td>Viscosity</td>
<td>5 mPa.s</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>0.2 (wt%)</td>
</tr>
<tr>
<td>Waxes</td>
<td>2.7 (wt%)</td>
</tr>
</tbody>
</table>

Table 4.2. *Hazardous ingredients in COREXIT 9500* (Nalco, 2012)

<table>
<thead>
<tr>
<th>Hazardous Ingredients</th>
<th>(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillates, petroleum, hydrotreated light</td>
<td>10.0-30.0</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>1.0-5.0</td>
</tr>
<tr>
<td>Dioctyl sodium sulfo succinate</td>
<td>10.0-30.0</td>
</tr>
</tbody>
</table>

Table 4.3. *Physical Properties of COREXIT 9500* (Nalco, 2012)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.95 kg/m³ at 15.6 °C</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
</tr>
<tr>
<td>Viscosity</td>
<td>177 cps at 0 °C</td>
</tr>
<tr>
<td></td>
<td>70 cps at 15.6 °C</td>
</tr>
<tr>
<td></td>
<td>21 cps at 40 °C</td>
</tr>
<tr>
<td>Pour point</td>
<td>&lt;-57 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>147 °C</td>
</tr>
<tr>
<td>Flash point</td>
<td>83 °C</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>15.5 mmHg at 37.8 °C</td>
</tr>
</tbody>
</table>

**Interfacial Tension**

Interfacial tension, \( \sigma \), between the Oseberg Blend oil and synthetic seawater was measured to be 11 dynes per cm with the DuNouy tensiometer. At DORs \( \geq 1:1000 \), it was difficult to perform repeatable measurement of \( \sigma \) with the instrument since the indicated values were less than or equal to the smallest gradation on the Vernier dial.
This was confirmed independently with a spinning droplet test, where IFT (Interfacial Tension) for a 1:1000 DOR was measured to be less than 0.03 dyne/cm (Owoseni, 2014).

**Viscosity and Density**

Following the methods described in Chapter 3, the density and dynamic and kinematic viscosities of the Oseberg Blend oil and COREXIT 9500 were measured at different temperatures and DORs. The results are presented in Table 4.4 and Table 4.5, respectively. These data are plotted in Figure 4.1 - Figure 4.3.

*Table 4.4. Properties of COREXIT 9500 at different temperatures*

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>ρ [kg/m³]</th>
<th>μ [Pa-s] x 10³</th>
<th>ν [m²/s] x 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>952.2</td>
<td>61.571</td>
<td>64.663</td>
</tr>
<tr>
<td>30</td>
<td>944.4</td>
<td>36.741</td>
<td>39.118</td>
</tr>
<tr>
<td>40</td>
<td>936.6</td>
<td>23.72</td>
<td>35.327</td>
</tr>
</tbody>
</table>

*Table 4.5. Properties of Oseberg Blend crude oil mixed with COREXIT 9500 at different DOR and temperatures.***

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>ρ [kg/m³]</th>
<th>μ [Pa-s] x 10³</th>
<th>ν [m²/s] x 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DOR = 0</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>839.9</td>
<td>5.2404</td>
<td>6.2395</td>
</tr>
<tr>
<td>30</td>
<td>832.5</td>
<td>4.0684</td>
<td>4.887</td>
</tr>
<tr>
<td>40</td>
<td>825.2</td>
<td>3.0889</td>
<td>3.7431</td>
</tr>
<tr>
<td><strong>DOR = 1:500</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>842.1</td>
<td>5.4306</td>
<td>6.4492</td>
</tr>
<tr>
<td>30</td>
<td>834.8</td>
<td>4.2103</td>
<td>5.0434</td>
</tr>
<tr>
<td>40</td>
<td>827.3</td>
<td>3.2149</td>
<td>3.886</td>
</tr>
<tr>
<td><strong>DOR = 1:50</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>843.9</td>
<td>5.695</td>
<td>6.7487</td>
</tr>
<tr>
<td>30</td>
<td>836.5</td>
<td>4.4391</td>
<td>5.3071</td>
</tr>
<tr>
<td>40</td>
<td>829.0</td>
<td>3.3752</td>
<td>4.0714</td>
</tr>
</tbody>
</table>
Figure 4.1. Density of COREXIT 9500 and Oseberg Blend crude oil mixtures as a function of fluid temperature.

Figure 4.2. Dynamic viscosity of COREXIT 9500 and Oseberg Blend crude oil mixtures as a function of fluid temperature.
Streamwise velocity in the cylindrical observation section of the water tunnel was measured at five radial locations 7.5 cm downstream from the exit of the contraction. Four different pump settings (i.e., controller frequencies), which spanned the range of flow rates typically employed in the water tunnel experiments, were tested. Three replicates, comprising ensembles of about 500 velocity measurements, were performed at each location. Particle velocities were weighted by the LDV program according to their gate-time interval, and averaged for each replicate. Gate-time interval velocity weighting takes into account that faster particles will be more likely to pass through the measurement volume than slower particles. Table 4.6 presents the results of the LDV measurements. The reported mean, V, and RMS, $u_{rms}$, velocities in the Table are the
average values of the ensemble statistics calculated for each of the three replicates.

Intensity, $I = \frac{u_{rms}}{V}$, is also included. The complete velocity data set for all replicates is provided in Appendix A.

Table 4.6. Average and rms streamwise velocity for four different pump controller frequencies

<table>
<thead>
<tr>
<th></th>
<th>15 Hz</th>
<th></th>
<th>18 Hz</th>
<th></th>
<th>20 Hz</th>
<th></th>
<th>30 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ (mm)</td>
<td>$V$ (m/s)</td>
<td>RMS (m/s)</td>
<td>Int (%)</td>
<td>$V$ (m/s)</td>
<td>RMS (m/s)</td>
<td>Int (%)</td>
<td>$V$ (m/s)</td>
</tr>
<tr>
<td>0</td>
<td>0.114</td>
<td>0.019</td>
<td>16.89</td>
<td>0.136</td>
<td>0.011</td>
<td>7.743</td>
<td>0.139</td>
</tr>
<tr>
<td>0.3175</td>
<td>0.113</td>
<td>0.017</td>
<td>14.76</td>
<td>0.135</td>
<td>0.011</td>
<td>7.994</td>
<td>0.140</td>
</tr>
<tr>
<td>0.635</td>
<td>0.112</td>
<td>0.018</td>
<td>16.04</td>
<td>0.132</td>
<td>0.016</td>
<td>11.75</td>
<td>0.138</td>
</tr>
<tr>
<td>0.9525</td>
<td>0.101</td>
<td>0.019</td>
<td>18.44</td>
<td>0.130</td>
<td>0.018</td>
<td>13.72</td>
<td>0.135</td>
</tr>
<tr>
<td>1.113</td>
<td>0.088</td>
<td>0.021</td>
<td>24.15</td>
<td>0.115</td>
<td>0.017</td>
<td>14.5</td>
<td>0.125</td>
</tr>
</tbody>
</table>

Mean velocities given in Table 4.6 were non-dimensionalized using space-averaged (i.e., plug flow) velocities determined from the flow meter data and are plotted in Figure 4.4. The profiles extend over the entire observation section diameter. Radial symmetry and the no-slip condition at the wall have been assumed. Error bars shown for the 18 Hz pump frequency case were determined from the measured RMS velocity data. Table 4.7 summarizes the space-averaged velocities calculated from the flow velocity data for the four pump frequency cases. The table also reports the pipe Reynolds number based on the space-averaged velocity, i.d. of the observation section, and kinematic viscosity of the synthetic seawater.

Table 4.7. Space-averaged velocities

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.74</td>
<td>0.092</td>
<td>2240</td>
</tr>
<tr>
<td>18</td>
<td>0.89</td>
<td>0.111</td>
<td>2700</td>
</tr>
<tr>
<td>20</td>
<td>0.98</td>
<td>0.122</td>
<td>2970</td>
</tr>
<tr>
<td>30</td>
<td>1.42</td>
<td>0.177</td>
<td>4308</td>
</tr>
</tbody>
</table>
Figure 4.4. Non-dimensionalized velocity profiles in the water tunnel observation section for four different pump speeds. Error bars for the 18 Hz pump controller frequency case were estimated from the RMS velocity data.

As seen in Figure 4.4, the streamwise velocity field in the observation section is relatively uniform across most of the flow area, particularly at the higher flow rates, and the boundary layers are rather thin. This flat profile is desirable to minimize shearing forces acting on the droplets.

As seen in Table 4.6, the velocity fluctuation intensity, I, ranged from about 5% to 25%, with higher values typically occurring close to the wall. This level of velocity fluctuations was larger than anticipated. A few dye injection tests were performed but the results were unremarkable: the streams of dye were not observed to spread rapidly such as would be expected if the flow were turbulent. It is believed that the high fluctuation intensities arise primarily from pump frequency controller chatter (i.e., non-
steady seawater flow rates) and, at least near the boundary layers, from spatial variations in velocity over the finite optical sample volume.

According to the manufacturer, the gear pump driven by a steady motor will produce essentially pulseless flow; however, our controller utilizes pulse width modulation (PWM) to vary the motor speed. PWM employs on-and-off pulses (i.e., square waves) to mimic sine waves. This approximation is not perfect and results in a certain amount of motor chatter and, therefore, variations in flow rate.

Although the width of the LDV’s optical sample volume is constrained with an imaging slit, it is not a point and data are collected over a range of streamlines. As the sample volume moves closer to the wall and into the boundary layers, the data will average over the velocity gradient that falls within the volume. This, in turn, results in a broader velocity sample distribution with a larger RMS.
4.3 Droplet Evolution Results

Video recordings provided valuable qualitative insight into the effects of dispersant on the evolution of buoyant oil droplets. A collection of representative still video frames are reproduced below that identify key physical characteristics of the process. Next, GCMS chromatograms of water samples collected for tests conducted at different DORs are compared and the results are correlated with the video images.

As described in Chapter 3, all experimental results reported below were obtained for 1 ml quantities of mixtures of Oseberg Blend crude oil and COREXIT 9500 injected into approximately 30 liters of circulating synthetic seawater at 35 ppt salinity and temperatures between 25°C and 27°C. Several (8 hour) replicate experiments were performed at each DOR.

Video Images

The following figures are frame captures extracted from digital video recorded during the experiments. The time series represented by the images vary between the different DORs. Images are presented for each case up until the point where visible changes in droplet size ceased. An additional image is included in each set 4 or 8 hours after injection. At a given DOR, similar qualitative behavior was observed between all replicates. The scale on the bottom right of all images is equivalent to 5 mm.
1:50 DOR Case

Figure 4.5 through Figure 4.11 show the evolution of droplet size for the case where DOR = 1:50.

Figure 4.5. 1:50 DOR case 5 seconds after injection.

Figure 4.6. 1:50 DOR case 10 seconds after injection. Tip streaming can be seen from the large droplet, as well as from the smaller droplets at top center.
Figure 4.7. 1:50 DOR case 30 seconds after injection. The large droplet has decreased in size.

Figure 4.8. 1:50 DOR case 1 minute after injection.
Figure 4.9. 1:50 DOR case 5 minutes after injection.

Figure 4.10. 1:50 DOR case 30 minutes after injection.
At a DOR of 1:50, the larger droplets that formed during the injection of the oil sample assumed the shape of a downward-facing half or crescent moon and quickly shed small streamers of oil (hereafter referred to as “tip streaming”). Some of these filaments formed tiny droplets. Within 30 minutes, the ensemble of droplets in the water tunnel became essentially invisible to the naked eye and to the video camera at the magnification shown in the images. While “invisible” is a qualitative metric which depends on a number of factors, such as intensity and orientation of lighting, contrast, etc., a rough rule-of-thumb is that the eye can resolve objects with sizes of the order of 0.05 – 0.1 mm. Note that the larger black spots seen in Figures 4.10 and 4.11 are oil droplets that deposited on the tunnel walls.
1:100 DOR Case

Figure 4.12 through Figure 4.15 show the evolution of droplet size for the case where DOR = 1:100.

Figure 4.12. 1:100 DOR case 10 seconds after injection. Larger droplets formed than in the DOR = 1:50 case and their shapes were less distorted by drag forces.

Figure 4.13. 1:100 DOR case 1 minute after injection.
At a DOR of 1:100, droplets shrank rapidly via tip streaming for approximately 10 minutes. Thereafter, only very fine droplets remained. These small oil droplets were visible until the very end of the experiment (i.e., 8 hours after injection), unlike the 1:50 DOR case, in which all droplets eventually became undetectable to the naked eye.
**1:250 DOR Case**

Figure 4.16 through Figure 4.23 show the evolution of droplet size for the case where DOR = 1:250.

*Figure 4.16. 1:250 DOR case 10 seconds after injection.*

*Figure 4.17. 1:250 DOR case 20 seconds after injection.*
Figure 4.18. 1:250 DOR case 1 minute after injection.

Figure 4.19. 1:250 DOR case 2 minutes after injection.
Figure 4.20. 1:250 DOR case 10 minutes after injection.

Figure 4.21. 1:250 DOR case 15 minutes after injection.
A number of interesting droplet behaviors were observed in the 1:250 DOR experiments. At this DOR, the droplets evolved relatively slowly compared to the higher DOR cases, allowing for good imaging of tip streaming events. During tip streaming, the droplets gradually and noticeably shrank. There were also incidents of droplet breakup, where a droplet would tear into nearly equal pieces. Droplet shrinkage via streaming and tearing proceeded for about 15 minutes following injection. Thereafter, the remaining ensemble of droplets did not appear to evolve further.
1:500 DOR Case

Figure 4.23 through Figure 4.29 show the evolution of droplet size for the case where DOR = 1:500.

Figure 4.23. 1:500 DOR case 5 seconds after injection.

Figure 4.24. 1:500 DOR case 30 seconds after injection.
Figure 4.25. 1:500 DOR case 5 minutes after injection.

Figure 4.26. 1:500 DOR case 90 minutes after injection.
Figure 4.27. 1:500 DOR case 90 minutes after injection.

Figure 4.28. 1:500 DOR case 4 hours after injection.
At DOR of 1:500, only a limited amount of tip streaming was observed to occur for a short period of time before stopping. After a droplet stopped streaming, a gas bubble would sometimes form on the upper surface of the droplet which would grow over time. This phenomenon can be seen in Figure 4.27 and Figure 4.29. It could not be determined with the available data whether these bubbles comprised gas dissolved in the seawater that collected on the oil surface, or components of the crude oil that outgas from the liquid phase. The Oseberg Blend that was used in this investigation was a “dead” oil; i.e., it was supposed to have been degassed for safety reasons. Gas bubbles attached to the droplet surface were not observed when other oils were tested in the water tunnel.
1:1000 DOR Case

Figure 4.30 through Figure 4.33 show the evolution of droplet size for the case where DOR = 1:1000.

Figure 4.30. 1:1000 DOR case 5 seconds after injection.

Figure 4.31. 1:1000 DOR case 20 minutes after injection.
At DOR of 1:1000, no tip streaming was observed. The large droplets that formed from the injected oil would simply break apart into smaller droplets over time. At the end of the 8 hour experiment, there were numerous small droplets in the lower portion of the Imhoff cone, as well as gas bubbles in the upper viewing section that had formed on the large droplets and eventually broke free.
No Dispersant Case

Figure 4.34 through Figure 4.43 show the evolution of droplets of Oseberg Blend crude oil with no added dispersant.

Figure 4.34. No dispersant 1 minute after injection.

Figure 4.35. No dispersant 2 minutes after injection.
Figure 4.36. No dispersant 5 minutes after injection.

Figure 4.37. No dispersant 10 minutes after injection.
Figure 4.38. **No dispersant 15 minutes after injection.**

Figure 4.39. **No dispersant 20 minutes after injection.**
Figure 4.40. No dispersant 25 minutes after injection.

Figure 4.41. No dispersant 40 minutes after injection.
When no dispersant was mixed with the crude oil, the relatively large droplets that formed did not exhibit any tip streaming or other oil shedding behavior. As seen in Figure 4.35, a small gas bubble was again observed to form on the top of the droplet roughly 2 minutes after injection. Figure 4.36 through Figure 4.40 document the growth of this bubble over time, until it becomes about the same size as the droplet. The composite structure consisting of the bubble attached to the upper surface of the droplet wobbled erratically. Once the bubble grew sufficiently large (at around 30 minutes after
injection), the oil droplet tore away from the bubble and usually split into smaller
droplets during the process, leaving behind only a small volume of oil still attached to the
bubble. After about one hour, the size of both the oil droplets and gas bubbles appeared
to remain unchanged until the end of the experiment.
Table 4.8 summarizes the major observations about droplet evolution from the water tunnel experiments. In this table, Evolution Time represents the approximate period following injection during which significant changes occur in the size of the oil droplets. As noted above, in most of the tested cases, droplets initially would shrink via tip streaming or tearing events until they either became undetectable by the camera or attained a “stable” size distribution. The period that tip streaming was observed appeared to scale with DOR. The mechanism behind the apparent cessation of shrinkage is unclear, but may be due to a number of factors, including changes in the hydrodynamic stresses felt by the oil droplet as its diameter (and corresponding Reynolds number) decreases as well as a possible loss of dispersant from the bulk oil phase during tip streaming, which reduces the DOR in the remaining droplet.
Table 4.8. Observations regarding droplet behavior for different DOR

<table>
<thead>
<tr>
<th>DOR</th>
<th>Size of droplets generated by injection</th>
<th>Mode of droplet evolution</th>
<th>Evolution time</th>
<th>Condition of droplets at the end of the experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:50</td>
<td>Cloud of tiny droplets with a few larger ones</td>
<td>Tip streaming</td>
<td>~30 minutes until all droplets disappeared</td>
<td>Invisible</td>
</tr>
<tr>
<td>1:100</td>
<td>No cloud; numerous droplets &lt;1 mm</td>
<td>Tip streaming off of larger droplets</td>
<td>Tip streaming mostly ceased after ~15 minutes</td>
<td>A few droplets estimated to be of the order of $10^2$ μm remained</td>
</tr>
<tr>
<td>1:250</td>
<td>No cloud; droplets &gt; 1 mm formed</td>
<td>Tip streaming; tearing; gas bubble formation</td>
<td>Tip streaming and tearing mostly ceased after ~10 minutes</td>
<td>A few small droplets &lt; 1 mm remained</td>
</tr>
<tr>
<td>1:500</td>
<td>Droplets &gt; 1 mm formed; droplets are still deformed in shape</td>
<td>Minimal tip streaming; gas bubble formation and tearing</td>
<td>Tip streaming occurs for ~5 minutes. Gas bubbles formed around 1 hr. and led to wobbling and tearing</td>
<td>Medium sized droplets in the mm range remained</td>
</tr>
<tr>
<td>1:1000</td>
<td>Droplets &gt; 1 mm formed; droplets slightly deformed compared to no dispersants</td>
<td>No tip streaming observed; gas bubble formation and tearing</td>
<td>No tip streaming. Gas bubble starts forming at 10 min. Droplets formed during tearing smaller than no dispersant case.</td>
<td>Medium sized droplets in mm range remained.</td>
</tr>
<tr>
<td>0</td>
<td>Droplets &gt; 1 mm formed, droplets are elliptical with nice rounded edges</td>
<td>No tip streaming; gas bubble formation and tearing</td>
<td>Gas bubble starts forming at 2 min, tearing occurs around 30 min.</td>
<td>Medium sized droplets in mm range remained</td>
</tr>
</tbody>
</table>
4.4 Gas Chromatograph/Mass Spectroscopy Results

Hexane, the solvent used in the GCMS analyses, had a column retention time of around 10 minutes. Any hydrocarbon components collected by SPE from the seawater samples with similar retention times were overwhelmed by the strong solvent signal and therefore could not be resolved. It also was determined that the GCMS signal after about 25 minutes varied widely between some replicates and consequently these data are questionable. The reported results focus on hydrocarbons that elute between approximately 10 minutes and 25 minutes. This roughly corresponds to carbon numbers between about C8 and C20.

Triplicate samples for five DORs along with four controls were tested using the GCMS as described in Chapter 3. The five tested DORs were: 1:50, 1:100, 1:250, 1:500, and 1:1000. The controls were: solvent-only, 100 ppm toluene, oil-only, and dispersant-only.

In Figure 4.44, three chromatograms are overlaid; two of the signals correspond to separate 100 ppm toluene injection, and one signal represents a hexane-only injection. The large peak immediately after 10 minutes is due to toluene. This figure also illustrates the signal variability after 25 minutes.
Figure 4.44. Chromatograms for hexane-only (purple) injection and two 100 ppm toluene injections. The strong peak around 10 minutes corresponds to toluene.

Figure 4.45 presents the chromatograms of the water samples collected at the end of experiments in which only oil (1 ml) or only dispersant (0.02 ml, maximum injected dispersant at 1:50 DOR) was injected into the circulating water tunnel. Following convention, count/s is plotted against elution times. No hydrocarbon peaks are detected except for the toluene added to the solvent. In the absence of any added dispersant, no detectable quantities of the crude oil dissolve or are entrained into the seawater. COREXIT 9500 employs a light petroleum distillate solvent; however, the water sample collected when only dispersant was injected into the water tunnel does not show any hydrocarbon peaks.
Figure 4.45. Chromatograms of seawater samples from the oil-only and dispersant-only control experiments.

Figure 4.46 through Figure 4.50 present chromatograms for the five tested DORs. Three separate experiments conducted for each DOR are overlaid in each figure.

Figure 4.46. Chromatograms of the GCMS injections for the triplicate experiments at DOR of 1:50.
Figure 4.47. Chromatograms of the GCMS injections for the triplicate experiments at DOR of 1:100.

Figure 4.48. Chromatograms of the GCMS injections for the triplicate experiments at DOR of 1:250.
Figure 4.49. Chromatograms of the GCMS injections for the triplicate experiments at DOR of 1:500.

Figure 4.50. Chromatograms of the GCMS injections for the triplicate experiments at DOR of 1:1000.

It should be mentioned again that the seawater samples collected after 8 hours were obtained by diverting a portion of the seawater circulating through the flow loop while the pump was operating. Any tiny oil droplets that remained suspended in the observation section or Imhoff cone were therefore excluded from these samples; they contained no visible oil droplets.
The figures indicate reasonably good repeatability of the GCMS profiles between the triplicate experiments performed for each DOR case. At DORs ≥ 1:250 (i.e., 0.4% volume), significant hydrocarbon peaks are detected in the chromatograms. At 1:500 DOR, these peaks are barely visible above the background noise and almost disappear completely at 1:1000 DOR. These trends correlate well with the qualitative video observations that suggest that significant quantities of the injected oil persist in the water tunnel as visible droplets as DOR decreases below about 1:250.

To illustrate the changes in GCMS hydrocarbon signatures due to dispersant concentration, chromatograms corresponding to sequential DORs are compared in Figure 4.51 to Figure 4.55.

![Comparison of chromatograms for 1:50 (green) and 1:100 (purple) DORs.](image)

*Figure 4.51. Comparison of chromatograms for 1:50 (green) and 1:100 (purple) DORs.*
Figure 4.52. Comparison of chromatograms for 1:100 (green) and 1:250 (purple) DORs.

Figure 4.53. Comparison of chromatograms for 1:250 (purple) and 1:500 (green) DORs.
These data demonstrate the continuous and significant reduction in the amount of entrained and dissolved hydrocarbons in the seawater as the concentration of COREXIT 9500 mixed with the crude oil decreases. The figures also show that the elution times of the different peaks (which correspond to different hydrocarbon species) align well for all the DORs, which is expected since the same crude oil was employed in all tests.

4.5 Quantification of GCMS Results

It is desirable to quantify how the amount of hydrocarbons extracted from the seawater samples changed with DOR. Integrating the GCMS chromatograms would provide information on these amounts; however, the relatively large number of hydrocarbon species that appear in the chromatograms complicate this analysis. Normally, each species would require a standard for comparison to determine its concentration. Running standards for every detected species in these experiments was determined to be problematic. Moreover, identifying the specific hydrocarbons associated with each elution time is not always straightforward, which makes the
preparation of reference standards from commercially available reagents difficult. It was decided instead to determine the ratios of signal strength of all the major GCMS peaks (i.e., the area under the peaks) for different DORs relative to known dilutions of the tested crude oil.

Two dilutions of 1000 ppmV and 2500 ppmV of Oseberg Blend crude oil in hexane were prepared and injected into the GCMS. The areas under the major chromatogram peaks were then determined by integration and are compared in Table 4.9.

Table 4.9. Comparison of integrated chromatogram peaks for 2500 ppmV and 1000 ppmV dilutions of Oseberg Blend crude oil in hexane.

<table>
<thead>
<tr>
<th>2500 ppmV</th>
<th>1000 ppmV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min.)</td>
<td>Counts</td>
</tr>
<tr>
<td>10.111</td>
<td>3.44E+08</td>
</tr>
<tr>
<td>10.741</td>
<td>2.06E+08</td>
</tr>
<tr>
<td>11.098</td>
<td>1.36E+08</td>
</tr>
<tr>
<td>11.274</td>
<td>7.40E+07</td>
</tr>
<tr>
<td>11.860</td>
<td>3.77E+08</td>
</tr>
<tr>
<td>12.318</td>
<td>2.69E+08</td>
</tr>
<tr>
<td>13.851</td>
<td>3.18E+08</td>
</tr>
<tr>
<td>15.631</td>
<td>3.18E+08</td>
</tr>
<tr>
<td>17.240</td>
<td>2.78E+08</td>
</tr>
<tr>
<td>18.295</td>
<td>1.21E+08</td>
</tr>
<tr>
<td>18.717</td>
<td>2.46E+08</td>
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<tr>
<td>20.090</td>
<td>2.56E+08</td>
</tr>
<tr>
<td>21.377</td>
<td>2.19E+08</td>
</tr>
<tr>
<td>22.588</td>
<td>1.95E+08</td>
</tr>
<tr>
<td>23.737</td>
<td>1.88E+08</td>
</tr>
<tr>
<td>23.749</td>
<td>1.70E+08</td>
</tr>
<tr>
<td>24.821</td>
<td>1.70E+08</td>
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<tr>
<td>24.907</td>
<td>8.19E+07</td>
</tr>
<tr>
<td>25.853</td>
<td>1.66E+08</td>
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<tr>
<td>26.836</td>
<td>1.74E+08</td>
</tr>
<tr>
<td>27.796</td>
<td>1.36E+08</td>
</tr>
<tr>
<td>28.786</td>
<td>1.19E+08</td>
</tr>
<tr>
<td>29.846</td>
<td>9.23E+07</td>
</tr>
<tr>
<td>Average</td>
<td>2.51</td>
</tr>
</tbody>
</table>
The ratios of the areas under individual peaks that occur for elution times between about 10 minutes to 30 minutes in the respective chromatograms are provided in the column on the right. Although the ratios range from 1.95 to 3.15, the average value of these ratios is calculated to be 2.51, which corresponds to the ratio of the concentrations of the crude oil in the hexane. This suggests that the GCMS has a linear response to the components of the oil; i.e., the area under the peaks scales linearly with the total concentration of oil in the injected sample. If this instrument behavior is assumed to apply for our sample analyses, then this offers a relatively simple means to compare the results of the five DORs tested, and allows us to estimate the concentration of crude oil contained in the seawater at the end of an experiment.

The maximum possible concentration of oil in seawater for these experiments was ~33 ppmV. This assumes complete dissolution and dispersion of the 1 ml of injected oil into the 30,000 ml of circulating seawater, with no devolatilization or deposition. Since, however, the water tank and tunnel had to be washed after every test to remove oil residue from the walls, there was deposition. Furthermore, at some DORs, gas bubbles were observed escaping from the oil phase and, based on odors detected during the tests, it is likely that devolatilization of lighter hydrocarbon components dissolved in the water occurred at the water tank’s free surface.

Evidence of devolatilization during the 8 hour tests also can be seen in Figure 4.55 which compares the chromatograms of the 2500 ppmV Oseberg Blend in hexane and the 1:50 DOR experiment. The oil dilution chromatogram exhibits significant peaks at shorter elution times representative of lighter and generally more volatile hydrocarbons, while the 1:50 DOR experiment chromatogram is dominated by peaks for
(heavier and less volatile) hydrocarbon species that elute later. This shift in composition may be indicative of a loss of volatile species over the course of the water tunnel experiments.

![Figure 4.55](image)

*Figure 4.55. Comparison of chromatograms corresponding to the 1:50 DOR water tunnel experiment (green) and the 2500 ppmV Oseberg Blend (purple) injection.*

The peaks in the two chromatograms shown in Figure 4.55 were integrated and the ratios of these areas were calculated. The results are shown in Table 4.10. The strength of the first three peaks in the 2500 ppmV dilution chromatogram exceeded those in the 1:50 DOR results, but that was reversed at longer elution times. It is hypothesized that the lighter, more volatile, and slightly more soluble hydrocarbon species which tend to elute quickly, evaporated from the open top surface of the water in the water tunnel during the 8 hour experiments.
As indicated in Table 4.10, peaks strengths in the 1:50 DOR chromatogram were, on average, about 4.6 times greater than those in the 2500 ppmV dilution chromatogram. Since the SPE method results in a 2000X concentration of the collected hydrocarbons, it is estimated, by comparison with the 2500 ppmV dilution, that the seawater at the end of the experiment contained about 5.75 ppmV of oil (i.e., 2500 ppmV x 4.6/2000). A dilution of 5.75 ppmV of oil in the 30 L tank corresponds to 0.17 ml oil, suggesting that about 17% of the initial 1 ml of injected oil was dissolved or dispersed in the seawater at the end of the experiment. Since, at this DOR, no identifiable droplets were observed at the end of the test, it is assumed that the remainder of the oil was either deposited on the wetted surfaces of the system or devolatilized from the open free surface of the water in the tank.

<table>
<thead>
<tr>
<th>1:50 DOR time (min)</th>
<th>Counts</th>
<th>2500 ppmV time (min)</th>
<th>Counts</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.091</td>
<td>6.669E+07</td>
<td>11.098</td>
<td>1.361E+08</td>
<td>0.49</td>
</tr>
<tr>
<td>11.266</td>
<td>4.425E+07</td>
<td>11.274</td>
<td>7.397E+07</td>
<td>0.60</td>
</tr>
<tr>
<td>11.851</td>
<td>2.237E+08</td>
<td>11.86</td>
<td>3.772E+08</td>
<td>0.59</td>
</tr>
<tr>
<td>13.845</td>
<td>4.206E+08</td>
<td>13.851</td>
<td>3.178E+08</td>
<td>1.32</td>
</tr>
<tr>
<td>15.626</td>
<td>6.597E+08</td>
<td>15.631</td>
<td>3.179E+08</td>
<td>2.08</td>
</tr>
<tr>
<td>17.237</td>
<td>8.577E+08</td>
<td>17.24</td>
<td>2.779E+08</td>
<td>3.09</td>
</tr>
<tr>
<td>18.715</td>
<td>9.715E+08</td>
<td>18.717</td>
<td>2.460E+08</td>
<td>3.95</td>
</tr>
<tr>
<td>20.089</td>
<td>1.120E+09</td>
<td>20.09</td>
<td>2.560E+08</td>
<td>4.38</td>
</tr>
<tr>
<td>21.375</td>
<td>1.239E+09</td>
<td>21.377</td>
<td>2.186E+08</td>
<td>5.67</td>
</tr>
<tr>
<td>22.587</td>
<td>1.230E+09</td>
<td>22.588</td>
<td>1.949E+08</td>
<td>6.31</td>
</tr>
<tr>
<td>23.735</td>
<td>1.351E+09</td>
<td>23.737</td>
<td>1.883E+08</td>
<td>7.17</td>
</tr>
<tr>
<td>23.751</td>
<td>1.048E+09</td>
<td>23.749</td>
<td>1.698E+08</td>
<td>6.17</td>
</tr>
<tr>
<td>24.821</td>
<td>1.195E+09</td>
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<td>1.699E+08</td>
<td>7.03</td>
</tr>
<tr>
<td>24.907</td>
<td>6.436E+08</td>
<td>24.907</td>
<td>8.187E+07</td>
<td>7.86</td>
</tr>
<tr>
<td>25.853</td>
<td>1.075E+09</td>
<td>25.853</td>
<td>1.663E+08</td>
<td>6.46</td>
</tr>
<tr>
<td>26.836</td>
<td>1.094E+09</td>
<td>26.836</td>
<td>1.735E+08</td>
<td>6.31</td>
</tr>
<tr>
<td>27.797</td>
<td>8.096E+08</td>
<td>27.796</td>
<td>1.360E+08</td>
<td>5.95</td>
</tr>
<tr>
<td>28.787</td>
<td>7.264E+08</td>
<td>28.786</td>
<td>1.190E+08</td>
<td>6.10</td>
</tr>
<tr>
<td>29.847</td>
<td>5.628E+08</td>
<td>29.846</td>
<td>9.231E+07</td>
<td>6.10</td>
</tr>
</tbody>
</table>

AVERAGE: 4.61
To verify the estimated concentration of oil in the seawater, the 1:50 DOR results were compared with the results of the 1000 ppmV dilution injection. These data are shown in Table 4.11.

<table>
<thead>
<tr>
<th>1:50 DOR</th>
<th>1000 ppmV</th>
</tr>
</thead>
<tbody>
<tr>
<td>time (min)</td>
<td>Counts</td>
</tr>
<tr>
<td>11.091</td>
<td>6.669E+07</td>
</tr>
<tr>
<td>11.266</td>
<td>4.425E+07</td>
</tr>
<tr>
<td>11.851</td>
<td>2.237E+08</td>
</tr>
<tr>
<td>13.845</td>
<td>4.206E+08</td>
</tr>
<tr>
<td>15.626</td>
<td>6.597E+08</td>
</tr>
<tr>
<td>17.237</td>
<td>8.577E+08</td>
</tr>
<tr>
<td>20.089</td>
<td>1.120E+09</td>
</tr>
<tr>
<td>20.874</td>
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<td>7.264E+08</td>
</tr>
<tr>
<td>29.847</td>
<td>5.628E+08</td>
</tr>
</tbody>
</table>

Although, as indicated by the ratio of the areas of the individual peaks in the chromatogram, more hydrocarbon was always detected in the 1:50 DOR sample than the 1000 ppmV dilution, this excess increased with elution time, again suggesting a loss of the more volatile components of the oil. Peak strengths were, on average, 12.6 times greater in the 1:50 DOR chromatogram. Following the same approach as in the comparison with the 2500 ppmV dilution injection yields an oil concentration in the seawater of about 6.3 ppmV, suggesting that about 0.19 ml (19%) of the injected crude
oil was dispersed or dissolved. This compares reasonably well with the earlier value of 0.17 ml and supports the methodology.

Next, the 1:100 DOR test results are compared with the 2500 ppmV dilution injection data in Table 4.12.

Table 4.12. Comparison of integrated chromatogram peaks for 2500 ppmV dilution of Oseberg Blend crude oil in hexane and 1:100 DOR water tunnel experiment.

<table>
<thead>
<tr>
<th>1:100 DOR</th>
<th>Counts</th>
<th>2500 ppmV</th>
<th>Counts</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>time (min)</td>
<td></td>
<td>time (min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.734</td>
<td>4.155E+07</td>
<td>10.741</td>
<td>2.058E+08</td>
<td>0.20</td>
</tr>
<tr>
<td>11.092</td>
<td>1.734E+07</td>
<td>10.977</td>
<td>4.764E+07</td>
<td>0.36</td>
</tr>
<tr>
<td>11.268</td>
<td>1.020E+07</td>
<td>11.274</td>
<td>7.397E+07</td>
<td>0.14</td>
</tr>
<tr>
<td>11.853</td>
<td>6.708E+07</td>
<td>11.860</td>
<td>3.772E+08</td>
<td>0.18</td>
</tr>
<tr>
<td>12.312</td>
<td>3.277E+07</td>
<td>12.318</td>
<td>2.692E+08</td>
<td>0.12</td>
</tr>
<tr>
<td>13.844</td>
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<td>13.851</td>
<td>3.178E+08</td>
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</tr>
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Here again, the ratios indicate a loss of hydrocarbons with shorter elution times. The average peak strength in the 1:100 DOR chromatogram was about 0.49 times that detected in the 2500 ppmV dilution results. This yields an oil concentration in the seawater of 0.613 ppmV. At this concentration, 0.0184 ml, or 1.84% of the original 1 ml of crude oil was dispersed or dissolved into seawater after 8 hours. To verify this
calculation, the 1:100 DOR data are compared with the results of the more dilute 1000 ppmV GCMS injection in Table 4.13.

Table 4.13. Comparison of integrated chromatogram peaks for 1000 ppmV dilution of Oseberg Blend crude oil in hexane and 1:100 DOR water tunnel experiment.

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<tr>
<td>28.783</td>
<td>7.230E+07</td>
</tr>
</tbody>
</table>

| AVERAGE  | 1.26     |

These data indicate an average ratio of areas under the chromatogram peaks of 1.26, which corresponds to an oil concentration in seawater of 0.63 ppmV at 1:100 DOR. At this concentration, about 0.0189 ml or 1.89% of the 1 ml of injected oil was dispersed or dissolved. This compares well to the value of 1.84% determined by comparison with the 2500 ppmV dilution injection data.
At 1:250 DOR, droplets were observed to shrink via tip streaming and tearing for about the first 15 minutes and thereafter remain relatively stable in size. There were a significant number of small, but visible, droplets in the Imhoff cone at the end of the 8 hour experiment. As a consequence, the sampled seawater GCMS signal was weak and it was anticipated that the concentration of dissolved and dispersed oil would be low. Table 4.14 compares the strengths of the chromatogram peaks of the 1:250 DOR sample and the 1000 ppmV dilution injection.

<table>
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<tr>
<th>1:250 DOR</th>
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<th>Ratio</th>
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<td>time (min)</td>
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<td>time (min)</td>
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<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>0.29</strong></td>
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</table>

There is again an apparent loss of quickly-eluting hydrocarbons. On average, peak strengths were about 0.29 times those in the 1000 ppmV dilution injection results, yielding an oil concentration in seawater of about 0.15 ppm. At this concentration, only 0.0044 ml, or 0.44% of the original 1 ml of injected oil, was dispersed or dissolved.
The calculated concentrations were normalized using the data from the 1:50 DOR (0.02 or 2% by volume) tests and plotted against the DOR in Figure 4.56.

Finally, it was of interest to determine whether the hydrocarbon species detected by the GCMS were dissolved at the molecular level or represented tiny droplets fully entrained in the water phase. As described in Chapter 3, the samples drawn through the SPE frits were unfiltered. Although droplets could not be detected with the eye, the GCMS results indicated the presence of a number of heavier hydrocarbon species. The solubility of a compound in water is indicated by the octanol-water partition coefficient, $K_{o,w}$. The $K_{o,w}$ of a substance is defined as the ratio of the amount of that substance dissolved in octanol and in water at equilibrium. A compound with a $\log(K_{o,w})$ greater than 5.6 is considered to be insoluble in water. Many of the heavier hydrocarbon components that were detected in the GCMS chromatograms had $\log(K_{o,w})$ greater than 5.6.

To test whether the crude oil was being dissolved or dispersed, a series of 1:50 DOR experiments were performed in which a portion of the collected seawater sample
was filtered to remove dispersed oil prior to GCMS analysis. The remainder of the sample was analyzed as usual without filtering and the results were compared.

Figure 4.57 displays chromatograms of unfiltered seawater from two replicate experiments conducted at 1:50 DOR. Figure 4.58 presents chromatograms from the same experiments, but the sample seawater was filtered prior to SPE. A comparison of the filtered and unfiltered results is shown in Figure 4.59.

![Figure 4.57](image.png)

*Figure 4.57. Replicate chromatograms at 1:50 DOR; no filtering prior to SPE.*
The data suggest that filtering the water removes most of the detected hydrocarbons. This means that a large fraction of the hydrocarbons sampled from the water collected during the DOR experiments are dispersed as tiny droplets and not dissolved.
The limit of visibility of droplets in water is roughly 55 μm, although this depends on lighting and other factors. At 1:50 DOR, no droplets were visible in the water tunnel at the end of the 8 hour experiments. A sample of extracted water was analyzed using a Fraunhofer particle sizer for 1:50 DOR. The measured droplet size spectra and the corresponding cumulative volume distribution function are shown in Figure 4.60.

The entrained droplets have a bimodal particle size distribution, with a Sauter Mean Diameter of less than 1 μm. The largest droplets that were detected were about 50 μm, below the visible limit.
Conclusions and Suggestions for Future Work

Laboratory experiments were conducted to investigate the effects of DOR on the evolution of oil droplets during buoyant rise through seawater. Recent studies have reported that dispersants have a profound impact on the size distribution of droplets formed from the initial breakup of jets of crude oil discharging into seawater (Johansen, et al., 2013) (Brandvik, et al., 2013). Those studies determined that droplet size decreases with increasing DOR. Prior to the present study, however, no experiments had been performed to understand what happens to those droplets after they are formed. This is important, since anecdotal evidence from the DWH accident appear to indicate that while large oil droplets will surface and create a slick, small oil droplets can detrain from the buoyant contaminant plume to form subsurface intrusion layers that are not generally amenable to conventional clean-up techniques.

This investigation tested the following hypothesis: dispersants enhance the evolution of rising oil droplets, generally leading to a reduction in diameter over time, and the proportion of dispersant mixed into the oil phase is a primary parameter that controls this evolution.

Video from the experiments showed the extent to which crude oil droplets are affected by dispersants. With DORs of 1:50 and 1:100, the initial ensemble of droplets (typically < ~1 mm in diameter) would shrink over a period of 15-30 minutes via a “tip streaming” mechanism, where filaments of oil and dispersant are shed off the edges of a distorted droplet, until they could not be detected with the human eye or camera. As the DOR was increased to 1:500, tip streaming still occurred for a limited period of time immediately after injection, but a cloud of small droplets would remain in the observation
section and Imhoff cone once the tip streaming stopped. At DOR of 1:1000, tip streaming no longer occurred and droplets would only break up if other instabilities, such as those caused by presumed outgassing from the oil, were strong enough to provide the required energy.

GCMS analyses of seawater samples taken after circulating through the water tunnel for 8 hours supported the video observations. The data show a large increase in hydrocarbon content in seawater as a function of DOR. When comparing (unfiltered) chromatograms corresponding to the 1:50 DOR and 1:100 DOR tests (i.e., 2% and 1% dispersant by volume, respectively), the total amount of detected hydrocarbons decreased by approximately a factor of eight in the lower DOR sample. At 1:250 DOR (0.4% dispersant in oil by volume), hydrocarbon content was about 10% of the 1:100 DOR amount, suggesting a strongly non-linear relationship between DOR and the amount of hydrocarbons entering the seawater through dissolution and dispersion. No hydrocarbons were detected in the seawater samples of tests employing oil without dispersant and 1:1000 DOR. To determine whether the hydrocarbons detected in the seawater samples by the GCMS were dissolved or dispersed, an experiment was conducted at 1:50 DOR in which two 2000 ml samples were collected and one was filtered to remove fine (invisible) droplets before SPE. The GCMS chromatogram of the filtered sample had no discernable peaks, while the non-filtered sample displayed multiple and large peaks. This suggests that most of the hydrocarbons in the seawater after 8 hours of testing are largely dispersed and entrained rather than dissolved. Fraunhofer particle sizer data indicated that the unfiltered sample contains fine droplets with a Sauter diameter of <1 µm.
Comparison of the chromatograms of the original oil and dispersant mixtures and the mixture of dispersed hydrocarbons deposited on the SPE frits indicated significant differences in composition. The hydrocarbons dispersed in the seawater after 8 hours of testing had much higher fractions of heavier components than the original crude oil dilutions. This may be due to lighter hydrocarbon components dissolving into the seawater and evaporating off of the free surface at the top of the water tank which is exposed to ambient air.

The results of this study appear to confirm the hypothesis that the addition of dispersants to crude oil can significantly enhance the evolution of rising oil droplets, generally leading to a reduction in diameter over time. Moreover, this evolution is highly sensitive to the proportion of dispersant mixed into the oil phase.

Millimeter-scale oil droplets were observed to rapidly shrink under relatively mild hydrodynamic stresses associated with unrestrained buoyant rise, primarily via a tip-streaming mechanism. The droplets became invisible to the naked eye within the order of minutes. This corresponds to rise heights based on Stokes flow terminal velocities of roughly 150 m for a 2 mm droplet or 40 m for a 1 mm droplet over 30 minutes. Since droplets will shrink continuously, these distances are conservative estimates. At this point, droplets can probably be considered to be well-dispersed in the seawater and, based on plume model predictions, may detrain and form subsurface intrusion layers.

At lower DORs, tip streaming was observed to stop after an initial period of time. The period that tip streaming was observed appeared to scale with DOR. The mechanism behind the apparent cessation of shrinkage is unclear, but may be due to a number of factors, including changes in the hydrodynamic stresses felt by the oil droplet as its
diameter (and corresponding Reynolds number) decreases as well as a possible a loss of dispersant from the bulk oil phase during tip streaming, which steadily reduces the DOR in the remaining droplet.

It should be mentioned that, to date, there has been no experimental verification that the results of jet breakup tests conducted using small (i.e., 2-5 mm diameter) nozzles can be accurately scaled up to predict the oil droplet size distributions from seafloor oil spills. The present study seems to suggest that this scaling dilemma may not be significant if adequate dispersant is applied and mixed with the escaping oil near the break, since droplets produced by the initial jet breakup will rapidly shrink.

Further experimental research on the effects of DOR appears warranted. The following experiments should be considered:

- conduct tests at higher DOR to determine if a limit exists beyond which no further changes occur in the amount of hydrocarbons detected in the seawater with the GCMS;
- perform seawater extraction for hydrocarbon analysis at different time intervals to gain insight into temporal effects of DOR;
- for DORs < approximately 1:100, collect larger oil droplets after tip streaming ends to determine if there has been a loss of dispersant;
- conduct experiments at different seawater temperatures;
- conduct experiments at elevated pressures to study outgassing and other pressure-related phenomena;
- expand the range of crude oils tested;
• quantify dispersed droplet size (during and after the shrinkage phase), possibly with a Fraunhofer diffraction instrument or microscopy;

• modify the water tunnel to eliminate the free surface and contact with ambient air to prevent evaporation of light hydrocarbons.

• modify the water tunnel to collect any hydrocarbons evaporating at the surface
### Appendix A. LDV Velocity Measurements

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6 Works Cited


