A Fine Line Between Dispersion and Retention:
Oil-Sediment Interactions in Nearshore Marine Environments

by

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Abstract

When crude oil that is spilled in a marine environment approaches the shoreline, it can interact with suspended sediment to form either microscopic oil-mineral aggregates (OMAs), or macroscopic surface residual balls (SRBs) or submerged oil mats (SOMs). The formation of OMAs benefits oil spill remediation by naturally dispersing oil, while the formation of SOMs and SRBs can trap oil near the shore and lead to the re-oiling of beaches for years following a spill. OMAs, SRBs and SOMs all form in nearshore environments when oil interacts with sediment; yet, no relationships between them have been developed in current literature. This work strives to connect research between microscopic (OMAs) and macroscopic (SRBs and SOMs) aggregates of oil and sediment by systematically reviewing and analyzing literature regarding either size-class of aggregate with a specific focus on their formation, fate, and impacts in nearshore environments. Following this review, the results of a laboratory study to determine the effect of crude oil weathering on oil-mineral aggregation are presented. It is well accepted that oil needs to be highly weathered to form SRBs and SOMs, but there is currently a lack of understanding of how the weathering of oil will affect OMA formation. Based on literature, we identified two conflicting hypotheses: OMA formation 1) increases with weathering as a result of increased asphaltene and polar compound content; or 2) decreases with weathering as a result of increased viscosity. Controlled laboratory experiments were carried out to systematically test these two conflicting hypotheses. Experimental results using light, intermediate, and heavy oils, each at five weathering stages, show a decrease in OMA formation as oil weathers.

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This thesis is dedicated to my parents, Rachel and Gregory "Gus" Gustitus, without whom none of this would be possible. They raised me to always seek opportunities for growth and learning, and that foundation has been invaluable throughout my studies. Their constant encouragement, along with their unfailing love and faith in me, has helped me through countless trials, and continues to inspire me.

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List of Abbreviations

OMA   Oil-mineral aggregate

SRB   Surface residual ball

SOM   Submerged oil mat

LSC   Louisiana sweet crude

TIC   Texas intermediate crude

CHC   California heavy crude

ASW   Artificial seawater

Chapter 1:
Introduction

1.1 Background

Oil spills that affect sandy shorelines are of particular concern to remediation teams, governing agencies, local citizens, and affected industries because they may have severe long-term impacts on the local ecosystem and economy. Of particular interest to the oil spill remediation community are microscopic and macroscopic agglomerates that are formed from the interaction of oil with various types of sediments. These agglomerates mostly form in nearshore environments where sediment remains suspended in the water column, and breaking waves and other shoreline turbulent forces facilitate oil-sediment interactions. Microscopic agglomerates, which are commonly known as oil-mineral aggregates (OMAs), are typically < 1 mm in size, and are formed from interactions of oil with very fine sediments such as clay (Fitzpatrick et al., 2015; Gong et al., 2014; Sun and Zheng, 2009). Macroscopic oil-mineral agglomerates, often known as surface residual balls (SRBs), are formed from the interaction of weathered oil primarily with coarse sediments, such as beach sand, although they may also be formed with finer sediments, such as clay, or a combination of coarse and fine sediments (Michel et al., 2013). SRBs are typically either spherical or ellipsoidal, and are on the scale of a few centimeters. Large patches of floating oil can also interact with sediments to produce submerged oil mats (SOMs) which can reach up to several meters in length (Hayworth et al., 2015; Michel and Gait, 1995; OSAT-2, 2011). Once formed, SOMs

can be broken apart by various shoreline forces into centimeter scale fragments, which are then considered SRBs.

OMAs, SRBs and SOMs are the three main classes oil-mineral aggregates, and are classified using separate terminology primarily due to their differences in size. Apart from superficial classification by size, there is also a vast difference in how these microscopic and macroscopic aggregations are viewed by the oil spill remediation community. The formation of OMAs has been recognized as a mechanism that is favorable to oil spill remediation, since OMAs facilitate oil dispersion. This has led researchers to not only explore the natural occurrence of OMA formation, but also to seek engineered methods to facilitate the OMA formation process for dispersing spilled oil (Fitzpatrick et al., 2015; Sun and Zheng, 2009). On the contrary, the formation of SRBs and SOMs is considered detrimental to afflicted shorelines, since these agglomerates are difficult to remove, resulting in large amounts of submerged oil being trapped in the nearshore environment for indefinite periods of time (Dalyander et al., 2014; Yin et al., 2015). While the formation of OMAs can facilitate the rapid cleansing of oiled shorelines (Lee et al., 2003a), the formation of SRBs and SOMs can lead to the periodic re-oiling of afflicted shorelines for years following a spill (Dalyander et al., 2014; Plant et al., 2013). Additionally, dispersion of oil via OMA formation can facilitate natural weathering mechanisms including biodegradation (Jézéquel et al., 1999; Lee et al., 1996; Weise et al., 1999); on the other hand, formation of SOMs and SRBs leads to inhibition of natural weathering processes (Elango et al., 2014; John et al., 2016; Urbano et al., 2013; Yin et al., 2015).

1.2   Scope and Objective

This research focuses on developing connections between research on microscopic (OMAs) and macroscopic (SRBs and SOMs) aggregates in order to further the understanding of their formation, fate, and impacts in nearshore environments. In order to bridge the gap between research regarding these two size-classes of aggregates, a detailed review of relevant literature is presented. Several knowledge gaps are identified in this review; one such knowledge gap is that while it is well accepted that oil needs to be highly weathered to form SRBs and SOMs, there is currently a lack of understanding of how the weathering of oil will affect OMA formation. A bench-scale study carried out as part of this research clarifies the effect of crude oil weathering on OMA formation, which had previously been a source of disagreement in OMA literature.

1.3   Organization

This thesis is divided into four chapters including this introductory chapter. The remaining chapters are divided as follows:

Chapter 2 presents a detailed review of literature pertaining to microscopic (OMAs) and macroscopic (SRBs and SOMs) aggregates. Throughout this chapter, the current state of knowledge regarding these two classes of aggregates is compared and contrasted, with a specific focus on the formation, fate and impacts of these aggregates in nearshore environments. This chapter also identifies current knowledge gaps and makes recommendations for future collaboration between researchers that focus exclusively on either microscopic or macroscopic aggregates.

Chapter 3 details a bench-scale laboratory study that was completed in order to determine the effect of crude oil weathering on oil-mineral aggregation. Controlled laboratory experiments were carried out to systematically test between two conflicting hypotheses that had been identified in the literature, but had not previously been tested.

Chapter 4 summarizes the findings of this research, as well as the implications of this study, and includes recommendations for future research.

Chapter 2:
Comprehensive Review of the Formation, Fate and Impacts of
Microscopic and Macroscopic Oil-Sediment Agglomerates in Nearshore Marine Environments

2.1   Introduction

Although microscopic OMAs and macroscopic SOMs/SRBs are similar in composition, albeit not in size, they are rarely discussed simultaneously. Almost all recent reviews on this topic have focused exclusively on OMAs (Fitzpatrick et al., 2015; Gong et al., 2014; Loh et al., 2014; Loh and Yim, 2016; Sun and Zheng, 2009). Recently Warnock et al. (2015) reviewed the origin and fate of various types of macroscopic marine tar residues, including some discussion about SRBs that formed after the Deepwater Horizon oil spill; however, this study did not include any literature on microscopic residues. Furthermore, almost all published laboratory and/or field research efforts in this area focus exclusively on either microscopic or macroscopic oil-mineral aggregates. Since both OMAs (microscopic aggregates) and SOMs and SRBs (macroscopic aggregates) are simply different forms of oil-sediment agglomerates, we believe that researchers who focus solely on either microscopic or macroscopic aggregates could greatly benefit by understanding the research that has been carried out by the other group. Furthermore, we believe that the establishment of relationships between these two classes of aggregates can lead to a better understanding of the fate of oil in sandy beach environments. Therefore, one of the objectives of this review is to bridge the divide between these two areas and promote a more robust conversation. In this study, we review the current state of knowledge regarding OMAs, SRBs and SOMs with an
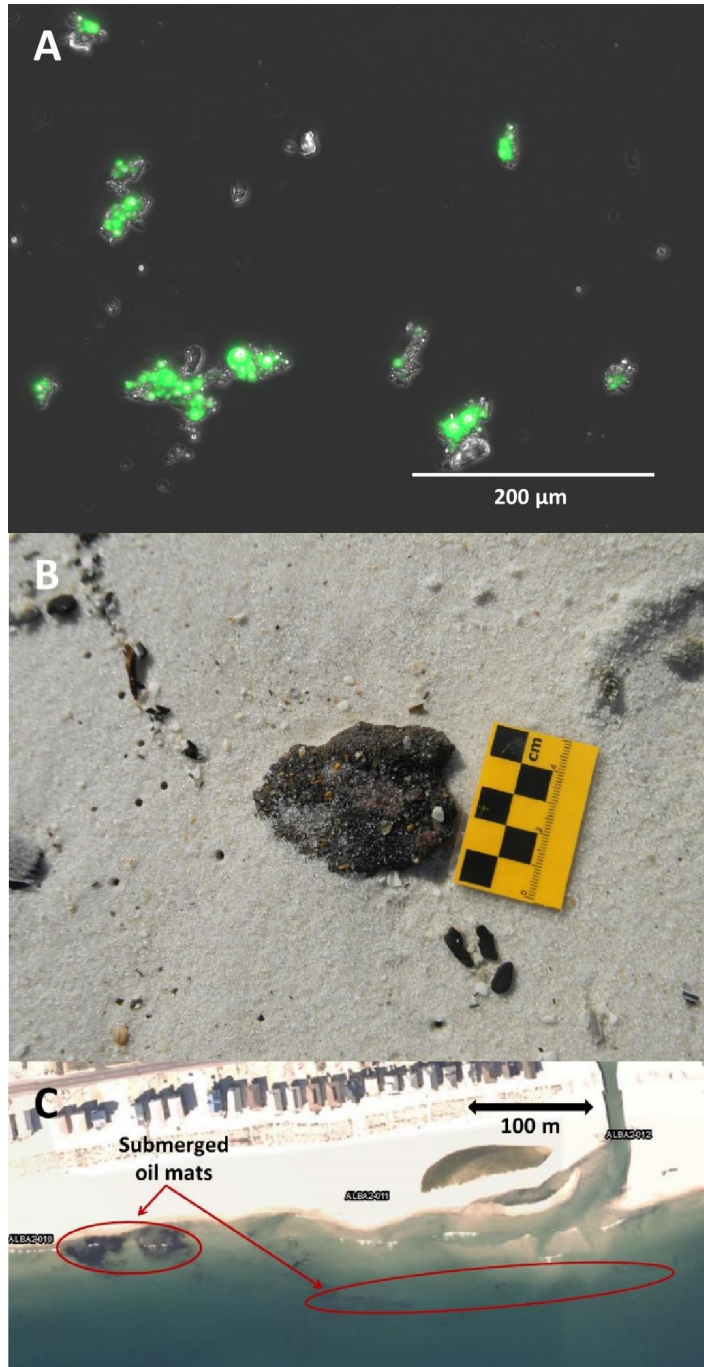
Figure 2-1. A) Oil-mineral aggregates (OMAs) viewed under fluorescent microscopy; B) a surface residual ball (SRB) on the beach; C) aerial image of a submerged oil mat (SOM) on the shoreline

aim to compare and contrast their implications for oil spill management, and to identify current knowledge gaps, particularly those pertaining to relationships between these two classes of aggregates. Throughout this chapter we will systematically review and analyze the differences between microscopic and macroscopic aggregates with respect to their formation, fate, and impacts in nearshore environments.

2.2   Terminology

Figure 2-2 shows a conceptual model of the various types of oil residues that may be present in nearshore environments. As shown in the figure, in addition to OMAs, SRBs and SOMs, several other types of floating oil spill residues can exist in nearshore environments. These include floating oil slicks that are typically thin layers of relatively fresh oil; thick layers of partially weathered oil in the form of emulsified mousse; oil stained sediment that does not form distinct agglomerates; and highly weathered pelagic tar balls. SRBs are considered a specific type of benthic tar ball, and as such are often discussed within the broad category of tar balls; however, the most common type of tar ball is pelagic (Warnock et al., 2015). Both pelagic tar balls and oil slicks primarily consist of oil with very little or no sediment incorporated in them; they may be found floating over nearshore waters, as well as either deposited atop or buried along beaches. This study focuses solely on aggregations of oil and sediment, and therefore oil slicks, pelagic tar balls, floating mousse or other tar material, and oiled sediments that are not aggregates are excluded from this discussion.

Aggregations of oil with material of biological origin (e.g. as bacteria, phytoplankton, dead cells or extracellular polymers) can form another type of oil spill residue, which is referred to as "marine oil snow (MOS)" (Daly et al., 2016; Fu et al., 2014). The formation of

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MOS is controlled by the presence of biologically mediated material such as the "sticky" exopolymeric substances (EPS), mucous-rich particles, and/or other dead cells (Passow, 2016; Quigg et al., 2016), rather than by the presence of purely inorganic mineral particulate material. Also, MOS is commonly observed in the open ocean (Daly et al., 2016). In this review we focus exclusively on the interactions of oil with inorganic sediment particles in nearshore environments; therefore, the formation of MOS is not covered in this review. However, MOS is an important topic that has garnered considerable interest following the Deepwater Horizon oil spill, and has recently been reviewed by Quigg et al. (2016).
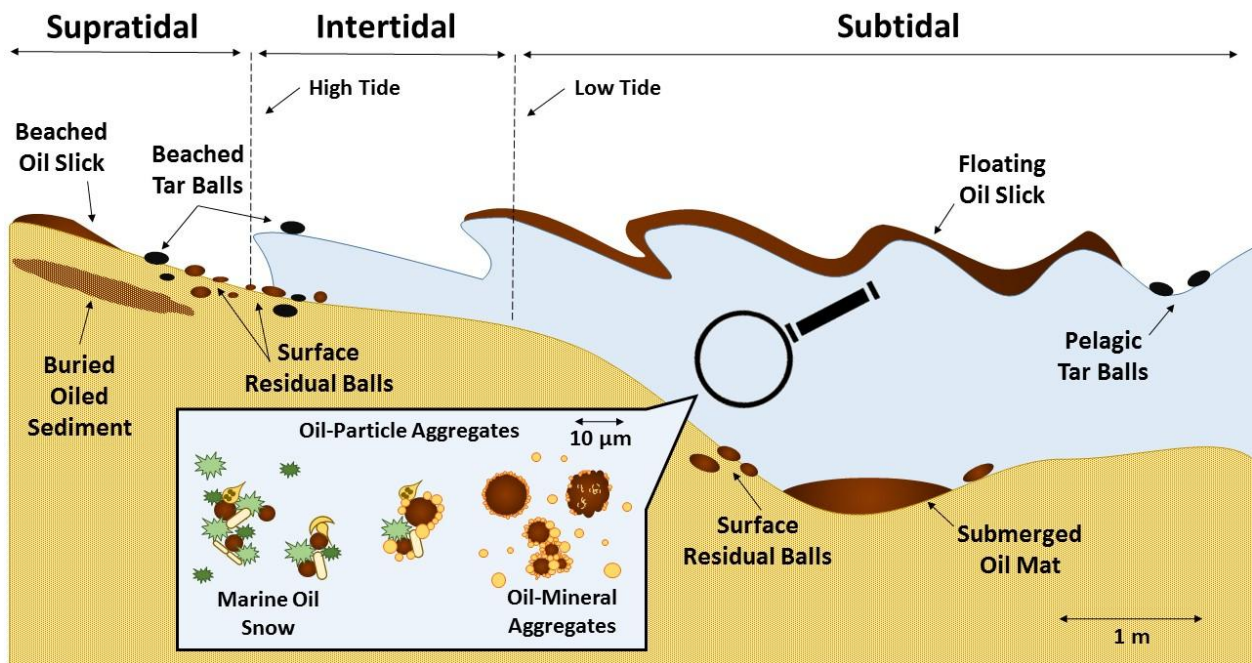
Figure 2-2. Conceptual model of the size and location of various oil residues found in nearshore environments.

2.2.1 Review of nomenclature used for describing microscopic aggregates

The terminologies used to describe different types of microscopic oil-mineral aggregates have varied greatly over the past few decades. One of the first studies that observed the adherence of oil to fine grained sediment was published by Poirier and Thiel (1941), which referred to the settled aggregates as an "oil-sediment-sea water mixture." Some subsequent studies examined oil/suspended particulate matter (SPM) interactions (Payne et al., 1987). However, this phenomenon did not garner significant attention until several decades after the Poirier and Thiel study, when researchers observed the natural cleansing of shorelines that had become oiled as a result of the Exxon-Valdez oil spill. These observations led to investigations on how the formation of microscopic aggregates could have contributed to the natural remediation (Payne, 1989). In a preliminary study that investigated the role of these aggregates in remediating the Exxon-Valdez spill, the term "clay-oil flocs" was first coined Bragg and Yang (1995). Since this study, research efforts aimed at understanding the formation of these aggregates has increased significantly. The term "oil-mineral aggregate (OMA)" was first used by Lee et al. (1998) to describe observations in both field and laboratory experiments where "fine grained sediment and oil combine to form micro-aggregates." Since then, the term OMA has been extensively used in several other published studies that focus on these oil-mineral interactions. A few later studies have also occasionally used the term "oil-sediment aggregate (OSA)" to refer to OMA (Bandara et al., 2011; Cai et al., 2016). More recently, some studies have used the terms "oil-suspended particulate matter aggregates (OSA)" (Gong et al., 2014; Loh et al., 2014; Sun and Zheng, 2009), or "oil-particle aggregate (OPA)" (Fitzpatrick et al., 2015; Zhao et al., 2016). However, OSA

and OPA are normally used in a more general context to describe oil interactions with inorganic minerals and/or organic particulates in the water column, although the term OSA has also been used in the past to refer to experimental results that produce standard OMAs (Khelifa et al., 2007; Khelifa et al., 2008; Sun et al., 2014; Sun et al., 2010).

2.2.2 Review of nomenclature used for describing macroscopic aggregates

Since macroscopic SRBs and SOMs are aggregates of oil and minerals (sand and/or fine clays), they have also been referred to as "oil-mineral (sand) aggregates" in the literature (Stout et al., 2016). However, it is important to recognize that the term OMA is primarily used to describe microscopic aggregates and is not intended to encompass any macroscopic aggregates. Therefore, a different nomenclature is necessary to clearly identify these two distinct size classes of aggregates. Until the Deepwater Horizon oil spill in 2010, SRBs were mostly lumped under the broad category of benthic tar balls since there was no uniform term to specifically describe them (Michel and Gait, 1995). Similarly, prior to the Deepwater Horizon spill, SOMs were referred to simply as tar mats or submerged sedimented oil (OSAT-1, 2010). The terms SRB and SOM primarily originated from the OSAT-2 report following the Deepwater Horizon spill. In this report, the term "small surface residual ball (SSRB)" was used to describe small oil-sand aggregate residues that escaped mechanical beach cleaning methods (OSAT-2, 2011). In later studies the term was condensed to "surface residual ball (SRB)" and used to describe oil residues on the scale of 1 mm – 10 cm that continued to wash ashore (Dalyander et al., 2014; Hayworth et al., 2015; Plant et al., 2013; Yin et al., 2015). Oil-sediment aggregates that range from 10 cm – 1 m (i.e. larger than an SRB and smaller than an SOM) have been referred to as "surface residue patties (SRPs)"

(Michel et al., 2013), or simply, "sand patties" (Aeppli et al., 2012; Stout et al., 2016). Aggregates similar to SOMs have been observed in beaches with coarse sediments (i.e. pebbles, gravels) that may or may not have sand as well. These aggregates are referred to as "asphalt pavements," since they form a hard crust of weathered oil on their exterior, which shelters less weathered oil on their interior (Owens et al., 2008). Another form of relatively dry SRBs is also found on dry beaches; these "beach-SRBs" are formed when washed out mousse was later covered by dry sand (Hayworth and Clement, 2011; Hayworth et al., 2011). The terms SRB, SRP, and SOM are currently almost exclusively used to describe Deepwater Horizon residues. Most recently, Dalyander et al. (2015) introduced the term "sand oil agglomerates (SOA)" to describe both SRBs and SOMs, and Bhattacharya et al. (2016) used the term "submerged residual oil mat (SRM)" in place of SOM.

2.2.3   Proposal of a unified nomenclature for describing oil-sediment agglomerates

"*It is often asserted that discussion is only possible between people who have a common language and accept common basic assumptions. I think that this is a mistake. All that is needed is a readiness to learn from one's partner in the discussion, which includes a genuine wish to understand what he intends to say. If this readiness is there, the discussion will be the more fruitful the more the partner's backgrounds differ.*" Popper (1963)

As discussed in the previous section, both microscopic and macroscopic aggregates have been referred to by several different names which can be confusing and at times misleading. For example, a study completed by Omotoso et al. (2002) on OMA formation was later cited by Goodman (2003) as an example of tar ball formation, which could be misleading. Figure 2-3 shows the various nomenclature used to describe different types microscopic and

macroscopic oil-sediment aggregates. In the spirt of Popper's statements, in this study we make an attempt to learn from various discussions and make recommendations to develop a uniform nomenclature, which can help promote better communication between different groups.
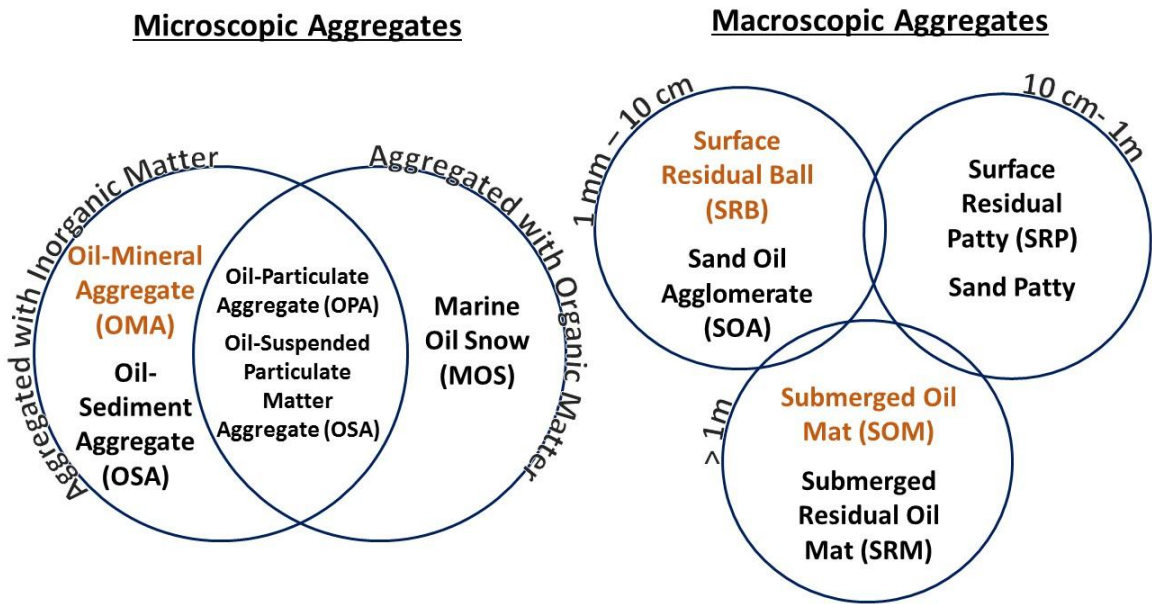
Figure 2-3. Terminology for referring to oil-sediment agglomerates. Terms highlighted in orange are used in this review to refer to the microscopic and macroscopic aggregates discussed here.

Due to the prevalent use of "OMA" to refer to microscopic aggregates, we recommend the continued use of this term to describe the aggregates of oil and inorganic minerals or sediments that are on a scale of 1 mm or less. Similarly, the term "oil-particulate aggregate (OPA)" is recommended to refer to microscopic aggregates of oil with both inorganic and organic particulates that are on a scale of 1 mm or less. For example, the term OMA can be used for laboratory experiments where oil and sediment are the only phases available for aggregation, but OPA can be used for field observations where it is impossible to remove the

possibility of aggregation with organic material, or in laboratory experiments where organic materials and minerals are simultaneously introduced.

Currently, the term "SRB" is used almost exclusively to describe benthic residues from the Deepwater Horizon oil spill. It is recommended that the use of this term be extended to describe similar oil spill residues formed from future oil spills when the aggregates are on the scale of ~1 mm - 10 cm. In order to clearly distinguish SRBs from traditional tar balls, we use the field observations made by various researchers (Mulabagal et al., 2013; Plant et al., 2013; Yin et al., 2015) and define their properties as: highly fragile (not rubbery); containing sticky, partially weathered oil; very high sediment content (~70% or more); and density values of ~1.6 g/cm^3 or more. The term SRB is preferred over the term "sand oil agglomerate (SOA)" because SRBs may also form with large quantities of clay or a clay/sand mixture. The less commonly used term, "surface residual patty (SRP)", is recommended to describe similar aggregates on the scale of ~10 cm - 1 m. SRPs are less common than SRBs, and are similar in composition, although they tend to have relatively fresh oil at their core. The term "SOM" is recommended to describe large, relatively immobile, sunken oil-mineral aggregates on the scale of several meters. This term is recommended for use over the term "tar mat", which is less specific.

Figure 2-4 summarizes our proposed nomenclature. In this review we have exclusively used these terms. We recommend that future studies should consider using this nomenclature with the spirit of promoting mutual learning and better understanding.
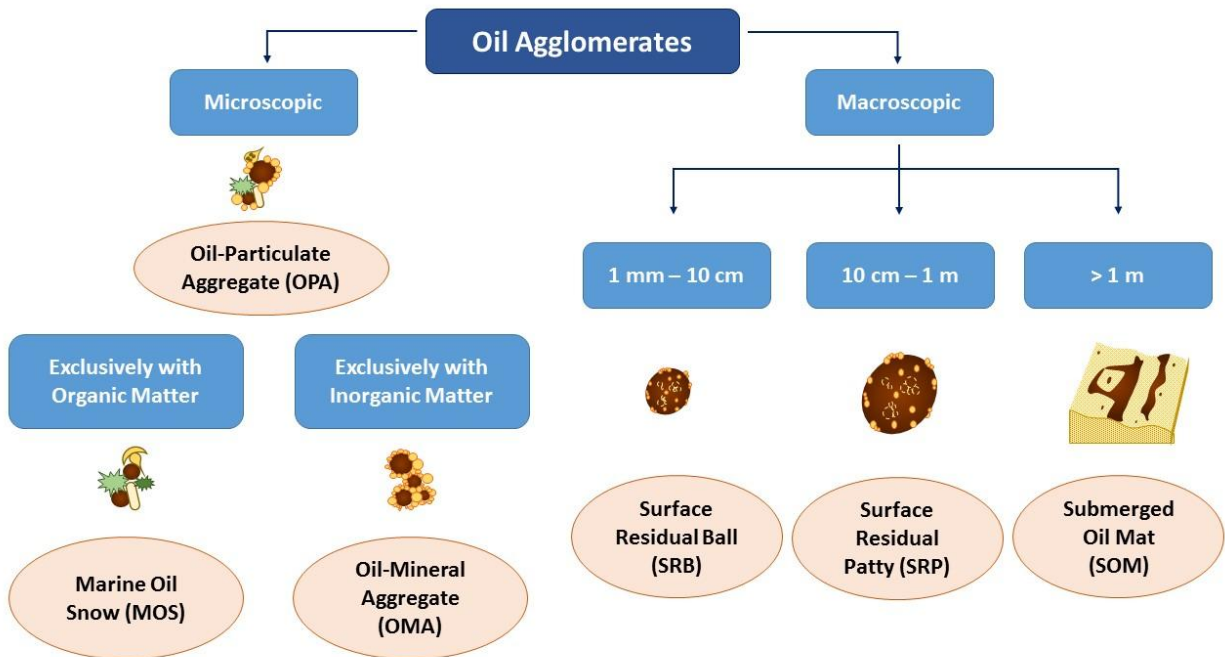
Figure 2-4. Recommended nomenclature for describing microscopic and macroscopic oil agglomerates that may be found in nearshore environments

2.3   Formation

Both microscopic and macroscopic aggregates are most commonly formed in nearshore environments, where high concentrations of suspended sediment and increased mixing energy from breaking waves facilitate aggregation processes. Over the past four decades, these aggregates have been observed and documented at several oil spill sites. In the section below we review several of these case studies, along with numerous laboratory studies, with an aim to compare and contrast our current understanding of how various types of microscopic and macroscopic aggregates formed in natural environments.

2.3.1 Formation of microscopic aggregates

OMAs characteristically form with very fine (typically < 10 µm) sediment particles (Sun and Zheng, 2009), and are more likely to form with fresh oils (Gustitus et al., 2017). As discussed previously, observations made following the Exxon-Valdez spill in 1989 first prompted the suspicion that OMAs may play a role in the natural remediation of oiled shorelines, which was verified by subsequent laboratory studies (Bragg and Owens, 1995; Bragg and Yang, 1995). Additional laboratory studies that were carried out using samples from the 1970 Arrow spill and the BIOS experimental site, which was oiled in 1981, showed that OMA formation could also have played a role in remediating these shorelines (Owens and Lee, 2003). The natural formation of OMAs in situ was first confirmed by microscopic observations made following the Sea Empress spill in 1996 (Lee et al., 1997). OMAs were also observed to play a significant role in the remediation of experimentally oiled beach plots that were part of the Svalbard shoreline field trials (Lee et al., 2003a; Sergy et al., 2003). In addition to marine environments, OMAs have also been observed to form in freshwater systems impacted by oil spills (Fitzpatrick et al., 2015).

In order for OMAs to form, spilled oil must first be dispersed into the water column as small droplets, following which the droplets must interact with and adhere to fine suspended minerals (see Figure 2-5). Nearshore environments are conducive to OMA formation because the energy dissipated from breaking waves can break oil slicks into droplets while simultaneously keeping fine sediment in suspension. Depending on the environmental conditions, as well as the properties of both the oil and sediment, OMAs may appear in

various sizes and shapes. Stoffyn-Egli and Lee (2002) identified and classified three main types of OMA: droplet, solid, and flake (see Figure 2-6). Droplet OMAs can form with either single or multiple droplets of oil. Single droplet OMAs consist of a single spherical droplet of oil stabilized by sediment particles, while multiple droplet OMAs contain several spherical oil droplets stabilized by sediment particles. Solid OMAs are aggregations of oil and mineral particles with irregular contours, where no clear individual droplets can be observed. Flake OMAs resemble membranes and are the least commonly observed type of OMA, having only been observed in laboratory experiments, and never in nature (Stoffyn-Egli and Lee, 2002). The size of an OMA is determined in part by its type. Droplet OMAs are typically a few μm wide, and grow larger as more droplets are incorporated; solid OMAs are on the scale of tens of μm, and can occasionally be found on the scale of hundreds of μm; flake OMAs are typically hundreds of μm and can stretch up to 1 mm in length (Stoffyn-Egli and Lee, 2002). The size of an OMA affects its buoyancy which determines how it is transported (i.e. rate of sedimentation or resurfacing). The size, type, and most importantly, the total amount of oil that will be dispersed as OMAs is highly dependent on a number of variables which can vary with environmental conditions (e.g. salinity, temperature, turbulence), the oil properties (e.g. viscosity, polar content) and/or the sediment properties (e.g. sediment concentration, hydrophobicity, particle size).
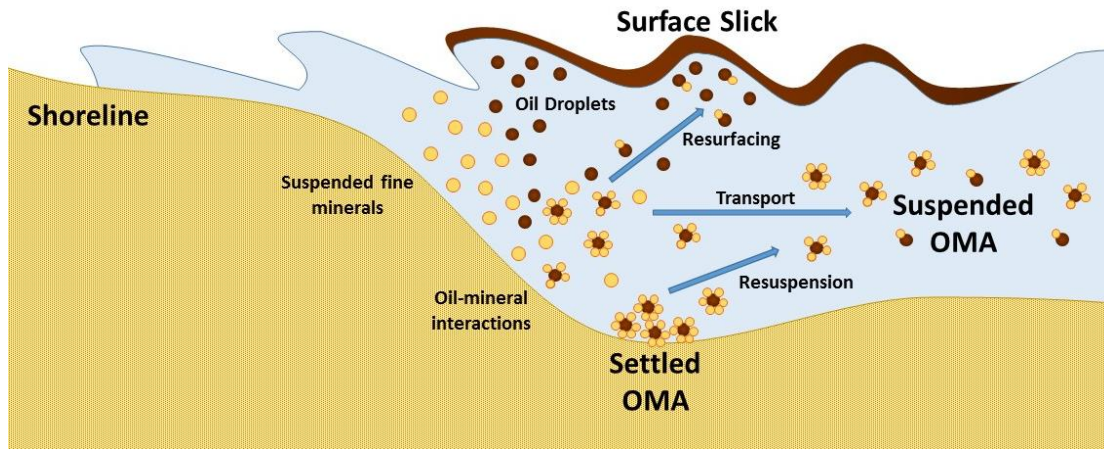
Figure 2-5. Conceptual model of how oil-mineral aggregates form in the nearshore environment adapted from Fitzpatrick et al., 2015
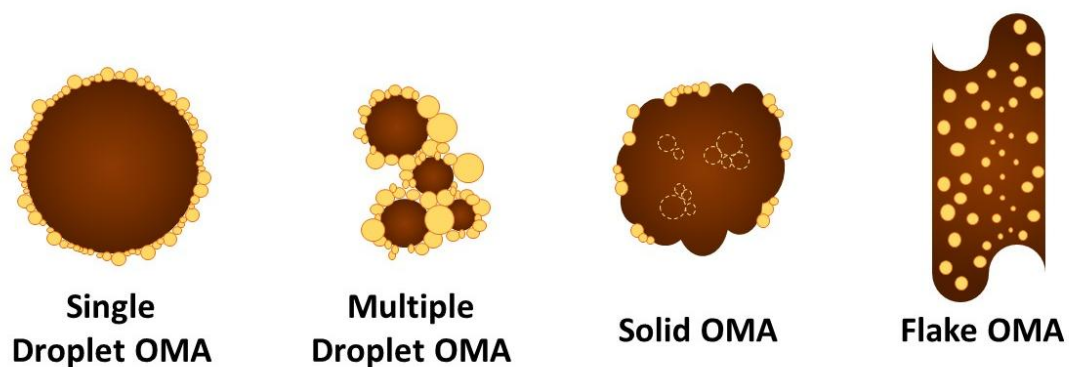
Figure 2-6. Conceptual models of oil (dark brown) aggregated with fine sediment (beige) in the form of droplet OMA, solid OMA and flake OMA. Adapted from Fitzpatrick et al. 2015 and Stoffyn-Egli and Lee, 2002.

Environmental factors such as salinity, turbulence and temperature can vary both spatially and temporally in nearshore environments such as estuaries and mangroves. In order to understand the effects of these changes, studies have been carried out to understand the impacts of these factors on OMA formation. One of the most important environmental factors that affects OMA formation is turbulence. The turbulence in a nearshore environment can vary significantly by location, and can also vary greatly within a single location based on local weather events such as storms. The energy dissipation rate is a key factor that controls the formation of OMAs, because it facilitates mixing by breaking down an oil slick into smaller droplets, and also keeps fine sediments in suspension. Typical values of energy dissipation rate per unit volume, e, for breaking waves are up to eight orders of magnitude higher than in the deep sea, which is why OMA formation is typically seen in nearshore environments as opposed to the open ocean (Delvinge and Sweeny, 1988). In environments with high mixing energy, OMA formation will be more efficient and will occur more rapidly than in calmer environments (Devadoss et al., 2009; Sun et al., 2014; Sun et al., 2010). At higher mixing energies, the droplets trapped in OMAs decrease in size (Sun et al., 2014). The mixing time, or the amount of time that the oil and sediment is subjected to turbulent conditions, also has an effect on OMA formation. Droplet stabilization in OMAs occurs relatively fast, typically taking less than 24 hours, and often occurring within 1-3 hours (Hill et al., 2002; Ma et al., 2008; Sun et al., 2010). Several studies have shown that the amount of oil dispersed as OMAs rapidly increases initially, but levels out over time (Payne et al., 2003; Sun et al., 2014; Sun et al., 2010). Ma et al. (2008) conducted mixing experiments to

demonstrate that once formed, OMAs tend to be stable, and can withstand continued exposure to turbulent conditions.

Other environmental factors that affect OMA formation include salinity and temperature. Salinity can vary seasonally and spatially in a nearshore environment, especially when there is a nearby discharge from a freshwater source. When oil is spilled in a freshwater system that discharges to the ocean, the potential to form OMAs can vary at different points as the oil is transported to increasingly saline conditions (Miranda et al., 2016). OMA formation will rapidly increase as salinity increases up to a critical salinity value, after which it will level off, and this critical salinity value is dependent on the type of oil and sediment present (Khelifa et al., 2003; Khelifa et al., 2005b; Le Floch et al., 2002). This critical salinity value might be as low as 0.15 ‰ (Le Floch et al., 2002) or as high as 35 ‰ (Khelifa et al., 2005b) depending on oil and sediment properties. This demonstrates why OMA formation is more effective in the marine environment than in freshwater systems, although OMAs have been shown to form in both systems (Fitzpatrick et al., 2015). At higher salinities, higher sediment concentrations are necessary for OMAs to begin to form (Guyomarch et al., 2002).

Temperature distribution at a spill site can vary greatly depending on the location and the season in which a spill occurs. OMA formation decreases with decreasing temperatures, and can be significantly limited in colder environments (Lee et al., 2012; Stoffyn-Egli and Lee, 2002); additionally, the size of OMAs increases with decreasing temperature (Wang et al., 2013). Temperature affects OMA formation because it influences the viscosity and adhesion properties of oil, which control the oil's ability to break into small droplets (Danchuk and Willson, 2011; Delvigne, 1987; Khelifa et al., 2002; Liu et al., 2006).

Different types of oil are unique in both chemical composition and physical properties, and these characteristics can significantly impact OMA formation processes. The viscosity of an oil controls the ability of that oil to disperse into microscopic droplets (Delvigne and Sweeney, 1988). Since droplets are necessary for OMA formation, increasing viscosity can result in a decrease in an oil's ability to form OMAs (Kepkay et al., 2002; Khelifa et al., 2002; Omotoso et al., 2002; Stoffyn-Egli and Lee, 2002). Contrarily, polar or charged components in the oil, such as asphaltenes, increase the attraction of the oil to charged surfaces such as clay, which will increase OMA formation (Bragg and Yang, 1995; Guyomarch et al., 2002; Sørensen et al., 2014). However, higher viscosity oils tend to also be associated with higher polar content, which can complicate predictions of OMA formation. Khelifa et al. (2002) developed an empirical approach for modeling the coupled effects of changes in viscosity and asphaltene content.

Chemical and physical oil properties vary, not just between types of oil, but also between weathering stages for a single type of oil. Weathering begins immediately following the release of an oil into the marine environment. Weathering processes such as evaporation, photodegradation, dissolution, biodegradation and emulsification will change the properties of the spilled oil over time. As lighter components leave the oil matrix, the overall viscosity and the polar content of the oil will increase. There are conflicting hypotheses in the literature regarding how oil weathering affects OMA formation. These hypotheses are that OMA formation 1) increases with weathering as a result of increased asphaltene and polar compound content (Bragg and Yang, 1995; Sørensen et al., 2014; Stoffyn-Egli and Lee, 2002); or 2) decreases with weathering as a result of increased viscosity (Payne et al, 2003).

Gustitus et al. (2017) recently demonstrated that as oil weathers, the oil's propensity to form OMAs can decrease significantly, suggesting that the negative effects of increased viscosity on OMA formation are greater than the positive effects of increased polar content as an oil weathers. Additionally, this study showed that even after several days of intense weathering, a significant amount of lighter crude oil could still be partitioned into OMAs, whereas after only one or two days of weathering the amount of heavy crude oil that formed OMAs dropped precipitously. This study is included as Chapter 3 of this thesis.

The physical properties of oil can be further altered through the use of chemical dispersants which are used in response to spills to increase oil dispersion into the water column. Chemical dispersants lead to increased concentrations and decreased sizes of oil droplets in the water column, which increases the likelihood of interactions between oil and fine minerals, and can thereby facilitate OMA formation (Khelifa et al., 2008; Li et al., 2007). The combined presence of chemical dispersants and mineral fines leads to more effective dispersion of oil than when either chemical dispersants or mineral fines are present alone (Li et al., 2007; Wang et al., 2013). When dispersants and mineral fines are present simultaneously, increased concentrations of chemical dispersant can lead to smaller, rounder OMAs, while increased concentrations of mineral fines can lead to larger, more irregular OMAs (Wang et al., 2013). Of concern however, is the fact that the simultaneous presence of chemical dispersant and mineral fines can greatly increase the amount of oil that is transported to the benthic zone through OMA formation (Cai et al., 2016; Khelifa et al., 2008).

In addition to variables related to the oil type and environment, the type, size and concentration of sediment can vary greatly between different nearshore environments, and will affect the formation of OMAs. Several studies have shown that OMA formation will increase with increasing sediment concentrations, at least until the concentrations of sediment and oil reach near equivalence, at which point OMA formation tends to reach its maximum efficiency (Ajijolaiya et al., 2006; Khelifa et al., 2007; Khelifa et al., 2008; Sun et al., 2010). Furthermore, the amount of OMAs formed is inversely proportional to sediment particle size (Ajijolaiya et al., 2006; Poirier and Thiel, 1941; Zhang et al., 2010). Sediment size also affects the buoyancy of OMAs, which are more likely to settle to the seabed when formed with larger sediments (Niu et al., 2014). The amount and type of suspended sediment not only affects the amount of oil trapped in OMAs, but also the size and type of OMAs that are formed (Cloutier et al., 2003; Guyomarch et al., 2002; Omotoso et al., 2002; Stoffyn-Egli and Lee, 2002). For example, Stoffyn-Egli and Lee (2002) observed that kaolinite and quartz produced droplet OMA, montmorillonite produced flake OMA, and Svalbard sediment produced solid OMA.

Recent studies have sought to identify the most effective sediment for OMA formation. Kaolinite has long been recognized as one of the most effective natural minerals for OMA formation (Poirier and Thiel, 1941; Wang et al., 2011; Zhang et al., 2010), although numerous other clays, including both natural clays collected from field sites and purified clays purchased from laboratory supply companies, have also been proven effective. Clays are more effective than other minerals, such as quartz, in part because they offer a greater surface area (Omotoso et al., 2002; Zhang et al., 2010). Additionally, hydrophobic minerals

have a greater tendency to form OMAs than hydrophilic minerals, and researchers have recently shown that the effectiveness of traditional minerals, such as bentonite and kaolinite, can be enhanced by altering their natural surface properties to increase their hydrophobicity (Chen et al., 2013; Lee et al., 2012; Wang et al., 2011; Zhang et al., 2010). Zhang et al. (2010) also explored the effectiveness of materials that would not typically be found in a beach environment, such as fly ash and graphite, but had limited success compared to traditional minerals. It is clear from these studies that sediment type and content can have a significant impact on OMA formation, just as environmental conditions and oil type can; therefore, all of these factors must be carefully considered when attempting to predict OMA formation in a nearshore environment.

Several researchers have attempted to create numerical models which can generate more robust predictions regarding OMA formation. These models utilize inputs such as oil content, sediment load, and environmental conditions to simulate the amount of OMA that will form (Bandara et al., 2011; Danchuk and Willson, 2011; Khelifa et al., 2005a; Sterling et al., 2004). The A-DROP model is a recently developed model which can be used to predict the amount of oil trapped in oil–particle aggregates (OPAs) (Zhao et al., 2016). A new conceptual framework for predicting oil–particle coagulation efficiency, that expanded on other established methods (Bandara et al., 2011; Hill et al., 2002; Sterling et al., 2004), was used to account for the effects of oil stabilization by particles, particle hydrophobicity, and oil–particle size ratio on OPA formation. A-DROP is generic model, which was developed with a goal to simulate OPA formation, and therefore it can model oil interactions with either organic or inorganic particles. The A-DROP model has been tested against experimental

observations and has also been used to simulate expected oil-sediment interactions in a typical nearshore environment. The model, however, lacks integration of key coastal dynamics important to OMA formation and transport. Effective models can help determine the extent to which natural OMAs can form in a given system, and help plan extensive remediation activities if necessary. When intervention is deemed necessary, model simulation results can be used to help determine the potential efficiency of remediation methods such as surf washing or sediment slurry application. Additionally, it is important to model the formation and transport of OMAs, because certain conditions could lead to their accumulation in bottom sediments where they could have a detrimental effect on benthic organisms (Niu et al., 2010; Niu et al., 2011).

2.3.2 Formation of macroscopic aggregates

Throughout the past several decades, there have been a plethora of surveys documenting the occurrence of pelagic oil spill residues, such as tar balls, whereas surveys on the occurrence of benthic oil spill residues, such as SRBs and SOMs, are lacking (Warnock et al., 2015). Michel and Gait (1995) is one of the studies that has documented some of the rare incidences of SRBs and SOMs formation from several spills across the globe. The Bouchard 155 spill that affected Tampa, FL in August, 1993 released a dense and viscous fuel oil which readily mixed with sediment and sunk after weathering. This resulted in several patches of SOMs and SRBs which became difficult to find as they were relocated or buried within the bottom sediment. Action was taken only to remove pieces of these aggregates that washed ashore, as it was assumed that the benthic ecological community would recover with time if no further action was taken to remove the SOMs (FDEP et al., 1997). A similar type

of heavy fuel oil was released in the Morris J. Berman spill that impacted San Juan, Puerto Rico in January, 1994. This oil sank and was buried in SOMs; however, some of this oil separated from the aggregates and reemerged each day to form a slick at the surface (Burns III et al., 1995). In November, 2002 the Prestige oil tanker spilled 70,000 tons of a high density oil off of the Galician coast of northwest Spain. Storm activity following this spill led to the formation of SRBs which were deposited in the intertidal zone and became buried when calm post-storm conditions facilitated the transport of sediment from the subtidal to the intertidal zone (Bernabeu et al., 2006). SRBs have also been deposited over several years along the south Gujarat coast of India, although their origin was not immediately obvious. Source identification techniques, such as chemical fingerprinting, revealed that the SRBs deposited in 2010 originated from tankers traveling nearby, while SRBs that were deposited from 2012-2014 originated from the Bombay High oil fields (Suneel et al., 2016; Suneel et al., 2015; Suneel et al., 2014).

Although SRBs and SOMs have resulted from several spills in the past, they received more attention after the Deepwater Horizon oil spill, which resulted in a large amount of SRBs and SOMs that continue to affect the GOM beaches to date (Clement et al., 2017; Hayworth et al., 2015; Nixon et al., 2016). Figure 7 shows a conceptual model describing the process that led to the formation of SOMs and SRBs near sandy beaches following the Deepwater Horizon oil spill. Unlike OMAs, which can form from both fresh or weathered oil, but are more likely to form from fresh oil (Gustitus et al., 2017), SRBs and SOMs are formed exclusively from emulsified weathered oil, commonly known as mousse. Mousse is denser and more viscous than fresh oil, but is not dense enough to sink without the

incorporation of additional foreign matter such as sand (Lee et al., 1989). In order for SOMs and SRBs to form, first the coastal dynamics facilitate the interaction of coarse sediment with mousse; this usually occurs near a sand bar where breaking waves suspend sediments and allow them to interact with the floating oil (see Step 1 in Figure 2-7). After accumulating a sufficient amount of sand, the density of the sand-mousse mixture will increase, causing it to sink (see Step 2 in Figure 2-7). After reaching the seafloor, the sunken mixture will accumulate additional sediment, forming SRBs and SOMs (see Step 3 in Figure 2-7). However, unlike OMAs, which are typically stable once formed, SRBs and SOMs can change shape or break apart into smaller pieces when exposed to continued turbulent conditions (Dalyander et al., 2014; OSAT-2, 2011).
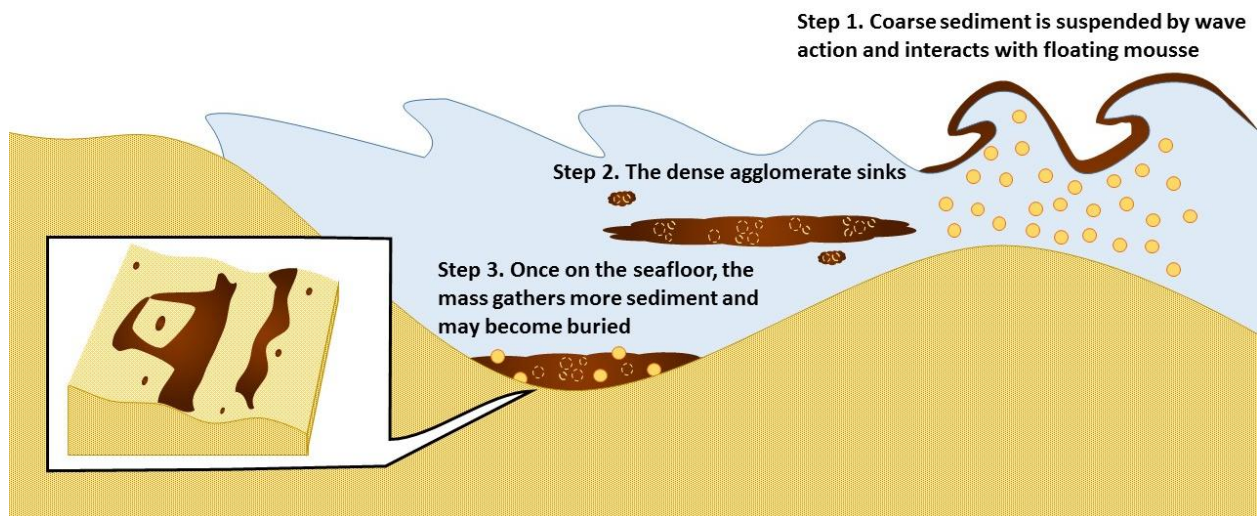
Figure 2-7. Conceptual model of how submerged oil mats and surface residual balls form in the nearshore environment adapted from Clement et al, 2017

Due to the magnitude of SRB and SOM contamination along the northern Gulf coast following the Deepwater Horizon spill, many studies have been carried out to understand the

distribution, transport dynamics, and physical and chemical characteristics of these aggregates, most notably in Louisiana (Elango et al., 2014; Lemelle et al., 2014; Urbano et al., 2013), Alabama (Clement et al., 2017; Hayworth et al., 2015; Wang and Roberts, 2013; Yin et al., 2015), and some in Florida (Wang and Roberts, 2013). SRBs resulting from this spill were typically found on the range of 0.5-8 cm in diameter, while SOMs spanned up to several meters in length and were up to 20 cm thick (Dickey and Huettel, 2016; Hayworth et al., 2015; Michel et al., 2013). SRBs and SOMs can be formed with highly weathered oil and either coarse sediment (such as the sand that is found along Florida and Alabama beaches) or large amounts of finer sediment (such as the clay that is found along some Louisiana beaches), and they can be found either atop the sediment layer or buried within the sediment, or can be washed up to rest in the supratidal zone. SRBs are often referred to colloquially as tar balls. They are different from traditional pelagic tar balls, which are rubbery with little or no sediment incorporated; SRBs, on the other hand, are a type of benthic tar ball that incorporates sand and/or clay, not only on the outer surface, but also throughout the interior. The SRBs and SOMs collected following the Deepwater Horizon spill had a high characteristic sand content ranging from about 83-97% (OSAT-2, 2011). In rare cases, the intense heating or burning of oil may cause residues to submerge (Moller, 1992), or the spilled oil itself might be denser than the receiving water (Michel, 2006). However, in the vast majority of cases the incorporation of sediment is required to sink oil in the nearshore environment (Michel and Gait, 1995; Warnock et al., 2015), and therefore the majority of benthic oil residues found in the nearshore environment are either SRBs or SOMs.

SRBs and SOMs are particularly challenging to remediation teams because they can be difficult to find, and can reappear on cleansed beaches weeks, months, or even years after a spill. Part of the reason that they can be difficult to find is because they are incorporated within more mobile sand beds, which leads to their periodic burial and exhumation (Dalyander et al., 2014; Plant et al., 2013). Since SRBs can be continuously formed by the fragmentation of SOMs, a dense accumulation of SRBs on a shoreline can be indicative of the presence of a large SOM in the nearby surf zone (OSAT-2, 2011). Figure 2-8 shows an accumulation of SRBs on the shore adjacent to an SOM that remains submerged. Angular SRBs are believed to be recently broken pieces of larger SOMs, while rounded SRBs are believed to either have formed during initial oiling or have broken off of an SOM a significant time ago and rounded from continued exposure to wave action over time (Dalyander et al., 2014; Hayworth et al., 2015). SOMs are typically found in the subtidal zone, while SRBs can be found in the subtidal, intertidal or supratidal zones (OSAT-3, 2013).

Figure 2-8. Surface residual balls (SRBs) accumulated on the shoreline next to a submerged oil mat (SOM) resulting from the Deepwater Horizon oil spill.

Numerical modeling tools have been used to better understand and predict the causes, hindrances, and patterns of the mobility of Deepwater Horizon SRBs along the Alabama/Florida coast (Dalyander et al., 2014; OSAT-3, 2013; Plant et al., 2013). These efforts employed the Delft3D coupled wave flow model which utilizes depth-averaged shallow water equations to examine how alongshore currents under various wave conditions would affect SRB transport (Dalyander et al., 2014; Plant et al., 2013). The various wave conditions that were used took into account wave height, direction, and period, as well as wind speed and direction. In order to determine SRB mobility, this study compared the shear

stress created by the coastal conditions with critical threshold values of incipient motion for SRBs. Modeling results revealed that while SRBs that are atop the seabed are mobile approximately 60% of the time, SRBs that are flush to the seabed, such as those that have recently broken off of SOMs, are unlikely to be mobilized under most hydrodynamic conditions. Additionally, the results showed that wave heights can play a significant role in the amount of shoreline that will be impacted by SRB mobility, with SRBs being mobile in small patches of the coast line for wave heights of 1-1.5 m and for long stretches of the coastline for wave heights of 1.5-2 m. As a result of these dynamics, it is unlikely that SRBs larger than 2.5 cm in diameter will be relocated under normal conditions, and will in fact be buried and exhumed periodically in the same location. However, storm events may uncover and redistribute larger SRBs up to 10 cm in diameter. This modeling study also revealed that coastal inlets accumulate SRBs in greater quantities than other shoreline features (Dalyander et al., 2014; Plant et al., 2013). In order to further verify the results of this study, Dalyander et al. (2015) generated artificial SRBs using paraffin wax and sand and released them in nearshore environments to observe their dynamics. This study found that the lowest estimations of critical stress that were used in the previous model are the best suited for predicting the movement of SRBs present on the surface of the seabed. Additionally, the largest artificial SRB (10 cm diameter, of ellipsoidal shape) became buried after only 10 minutes at a depth of 0.5 m of water, confirming the importance of accounting for burial and exhumation when predicting SRB mobility. It is hypothesized that the highest estimations of critical stress from the models are appropriate for partially buried SRBs (Dalyander et al.,

2014; Plant et al., 2013), but this was not confirmed by this study because the movement of buried SRBs was not observed.

There is also another class of SRBs, identified here as beach-SRBs, which are not of benthic origin. Beach-SRBs are formed when beached mousse is later covered by dry sand transported by wind, or partially wet sand deposited by storm surges. Figure 2-9a shows an example of a beach-SRB found in Orange Beach, Alabama, about 5 months after the Deepwater Horizon oil spill. Typically, these beach-SRBs are rather fragile agglomerates of oil and dry sand and can be easily broken apart and smeared into an oily layer, such as is the one shown in Fig 2-9b. The fate of beach-SRBs found along Pensacola beach in Florida has been extensively studied (Kostka et al., 2011; Rodriguez-r et al., 2015; Ruddy et al., 2014; Zuijdgeest and Huettel, 2012).
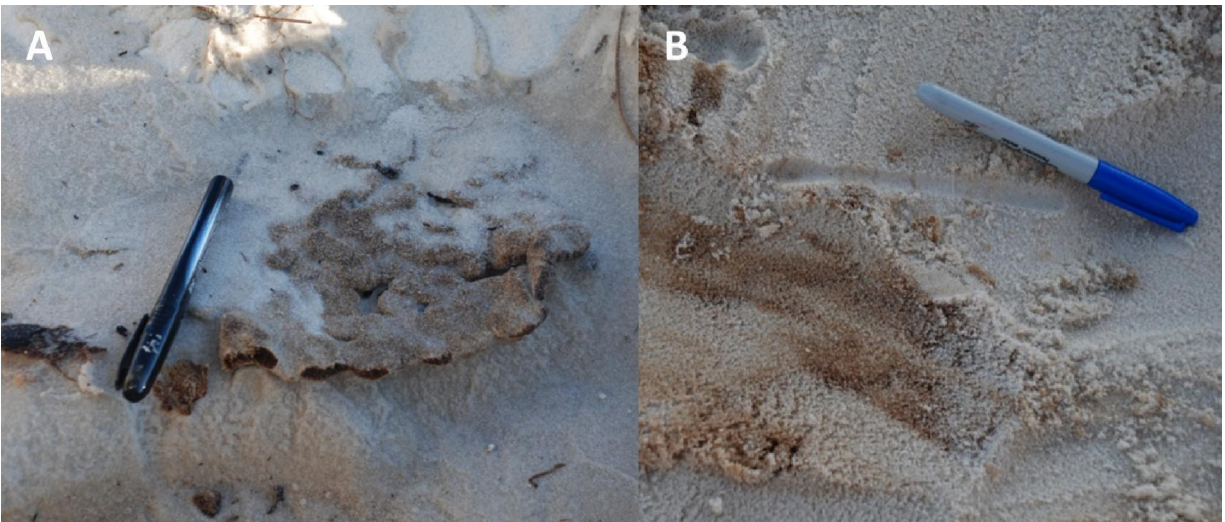
Figure 2-9. A) Beach-SRB buried after the Deepwater Horizon oil spill. B) Oily layer produced from a broken down beach-SRB following the Deepwater Horizon oil spill.

Based on field observations, it is accepted that in order for SRBs and SOMs to form, the oil must undergo sufficient weathering, including emulsion, before it is subjected to turbulent

conditions in a sediment-rich beach environment. For example, oil from the Deepwater Horizon spill weathered for anywhere from several days to several weeks on the open ocean before reaching sandy northern Gulf of Mexico shorelines where it sank and formed SRBs and SOMs (OSAT-2, 2011). However, in contrast to the plethora of lab studies that have been carried out to understand the formation dynamics of OMAs, there has been a dearth of lab work done to better understand the variables that affect SRB and SOM formation. A study by Savage and Ward (1984) attempted to synthesize tar balls under laboratory conditions by shaking oil, sand, and seawater in a tank under an artificial solar light source for a period of two months. All the tar balls produced in the study were buoyant tar balls, expect one which sank in seawater; this tar ball was produced using Yorba Linda crude oil collected from a California field. In this study, the chemical composition of the oil-sand mixtures was examined, but no information was derived on their physical properties or the dynamics involved in their formation. Lee et al. (1989) observed during laboratory studies that the incorporation of minerals into heavy oils could increase their density to above that of seawater, causing the oil to sink, but this work did not examine the formation of cohesive SRBs. Our review indicates that there is very little information available in the published literature that can help illuminate the extent to which oil, sediment, or environmental properties will affect the formation of SRBs and SOMs.

2.4   Fate

2.4.1   Weathering

Understanding natural weathering processes is an important aspect of oil spill science. Weathering can include various processes such as volatilization, emulsification,

biodegradation, photodegradation, and dissolution reactions. The vast difference in how macroscopic and microscopic aggregates are viewed by the oil spill remediation community stems from the dramatic dissimilarities in oil weathering rates that result from the differences in their sizes. For example, the formation of OMAs clearly facilitates rapid biodegradation, while the formation of SRBs and SOMs inhibits biodegradation, and thus can hinder the weathering of toxic components trapped in oil spill residues.

2.4.1.1 Weathering of oil in microscopic aggregates

The formation of OMAs following an oil spill is typically seen as beneficial to the affected environment, because OMAs can significantly enhance natural dispersion as well as oil degradation processes. There are two main mechanisms that make this possible. First, oil that is trapped in OMAs is in the form of micrometer-scale droplets, and is less likely to recoalesce with the surface slick or adhere to shoreline materials, thus increasing its overall available surface area (Bragg and Yang, 1995; Jahns et al., 1991; Owens, 1999). Second, OMA-entrained oil is associated with suspended particulates, which typically host greater numbers of microbes than the surrounding water (Harvey and Young, 1980; Van Loosdrecht et al., 1990). It is also well established that microbes that are attached to particles tend to be more metabolically active than those that are suspended in water (Harvey and Young, 1980; Hendricks, 1974; Kirchman and Mitchell, 1982).

Lab studies have demonstrated that OMA formation both accelerates and increases the biodegradation of spilled oil (Jézéquel et al., 1999; Lee et al., 1996; Weise et al., 1999). Lee et al. (1996) found that it took 28 days for untreated oil to achieve the same extent of oil degradation that was observed within one day by oil treated with mineral fines. Weise et al.

(1999) found that over 56 days, the fractions of n-alkanes and target aromatics remaining in oiled samples treated with mineral fines were significantly reduced compared to untreated samples. Microcosm studies on samples from a field trial where spilled oil was treated with mineral fines further confirmed enhanced degradation (Lee et al., 2011). This study also found that more than 56% of the treated oil was degraded after two months, despite the low temperatures in the ice-infested waters where the study took place. Furthermore, it has been posited that while the incorporation of oil into OMA would enhance the accessibility to the oil by microorganisms, it would also reduce the bioavailability and toxicity of the oil to larger aquatic organisms (Fitzpatrick et al., 2015).

2.4.1.2 Weathering of oil in macroscopic aggregates

Unlike the formation of OMAs, which enhances oil degradation rates, the formation of SRBs and SOMs can significantly hinder oil degradation rates (Pendergraft and Rosenheim, 2014). This could result in the oil trapped in SOMs and SRBs persisting in the environment for years following a spill. For example, published studies have documented the persistence of SRBs up to nine years after the Prestige oil spill (Bernabeu et al., 2013), and six years after the Deepwater Horizon oil spill (Clement et al., 2017). Typically, the oil that forms SRBs and SOMs undergoes significant weathering prior to reaching the shoreline, in some cases losing up to 50-60% of its mass, including many alkanes and polycyclic aromatic hydrocarbons (PAHs), as observed during the Deepwater Horizon oil spill (Liu et al., 2012; Stout et al., 2016). Therefore, oil that is derived from SRBs will always show reductions in alkanes, saturates, and PAHs compared to fresh oil; however, the reductions in the rate of degradation of these compounds have been the subject of many studies (Elango et al., 2014;

Evans et al., 2016; Gros et al., 2014; John et al., 2016; Stout et al., 2016; Urbano et al., 2013; Yin et al., 2015). Elango et al. (2014) measured PAHs, alkanes, and hopanes in Deepwater Horizon residues and found that the chemical composition of SOM samples collected more than a year after the spill was similar to that of first-arrival oil. However, this study also observed SRBs that had been transported to the supratidal or intertidal zones showed signs of consistent degradation of alkanes and lighter PAHs over that same time period. The persistence of oil compounds in SOMs can be explained by the anaerobic conditions and low nutrient content that characterizes these submerged masses (Elango et al., 2014; Urbano et al., 2013). In contrast, oil degrading microbes in supratidal SRBs benefit from aerobic conditions and higher (albeit, still relatively low) nutrient levels than SOMs, especially SRBs in the intertidal zone which are regularly inundated with seawater containing nitrogen (Elango et al., 2014). The degradation of SRBs and SOMs may be further influenced by the morphodynamic behavior of the afflicted beach, as was seen for SRBs resulting from the Prestige oil spill (Bernabeu et al., 2006; Bernabeu et al., 2009). When these SRBs became buried, the accumulated sediment exerted increased pressure on the residues, eventually breaking them down into smaller pieces. Although the burial slowed the microbial degradation of the SRBs, their fragmentation accelerated the natural remediation (Bernabeu et al., 2006).

The persistence of toxic PAHs within SRBs and SOMs is of particular concern and has been the subject of several studies related to Deepwater Horizon residues (Elango et al., 2014; John et al., 2016; Lemelle et al., 2014; Liu et al., 2012; Stout et al., 2016; Urbano et al., 2013; Yin et al., 2015). Yin et al. (2015) compared SRB samples from Alabama beaches

with a first-arrival mousse samples as well as with a reference MC252 crude oil sample. Comparison of fresh oil and mousse showed that various PAHs in the spilled oil weathered by about 45% to 100% while the oil was transported across the surface of the Gulf of Mexico; light PAHs, such as naphthalenes, were fully depleted, whereas heavy PAHs, such as chrysenes, were only partially depleted by about 45%. By comparing the SRBs with the first-arrival mousse, Yin et al. (2015) also showed that the concentrations of several heavy PAHs remained almost constant over a 4-year period (2010-2014), indicating that PAH weathering rates decreased significantly once the mousse was buried as SOMs and SRBs. Their study postulated that evaporation was most likely the primary weathering mechanism that weathered lighter PAHs, followed by photodegradation, which weathered heavy PAHs. The burial of SOMs and SRBs hindered sunlight exposure and inhibited photodegradation processes, a key degradation pathway for heavy PAHs (John et al., 2016). Experimental results by John et al. (2016) indicated that the weathering rates of several higher molecular weight PAHs slowed dramatically in buried oil spill residues, primarily due to the absence of sunlight. When these samples were homogenized and re-exposed to sunlight, the reactions were reactivated indicating that when natural processes fragment SOMs and re-expose them to sunlight, photodegradation reactions will indeed degrade heavy PAHs.

Biodegradation is another major pathway that can degrade PAHs in SRBs. Simister et al. (2015) isolated fungi from the Ascomycota phylum that were found Deepwater Horizon SRBs collected on Alabama shorelines and showed that isolates of this fungi could degrade both alkanes and PAHs, with a preference for lighter PAHs. Elango et al. (2014) analyzed both light and heavy PAHs and demonstrated that PAH degradation was limited in regions of

hypersaline conditions; however, PAH degradation was higher in supratidal SRBs where lower salinity levels were observed. Similar to the Yin et al. (2015) study, the Elango et al. (2014) study also noted that heavy PAHs were more resistant to degradation, and observed no significant changes in chrysene concentrations between the SRBs and first arrival mousse samples. It is expected that heavy PAHs, such as chrysene and its alkylated homologs, may remain trapped in SOMs and SRBs for many years (Yin et al., 2015).

While alkanes and PAHs degrade over time, oxygenated hydrocarbons (OxHCs) derived from degradation byproducts can increase in relative abundance within SRBs over time (Aeppli et al., 2012; Huba and Gardinali, 2016). A study by Aeppli et al. (2012) analyzed SRBs and other Deepwater Horizon samples and confirmed that OxHCs are formed, and not just preferentially enriched, as the oil weathers. They also determined that OxHCs are indeed formed from oil-derived carbon, and not from recently photosynthesized carbon. The formation of OxHCs was confirmed to have continued for four years following the Deepwater Horizon oil spill by White et al. (2016). OxHCs are recalcitrant once formed, and they are also difficult to quantify using standard analytical techniques. Much like heavy PAHs, OxHCs are expected to persist in the environment for many years and we currently do not fully understand the long-term impacts of these compounds.

2.4.2 Remediation

The goal of oil spill remediation efforts is to minimize environmental impacts, either by physically removing, or by rapidly dispersing and degrading as much of the oil as possible before it can cause harm to the environment. The formation of OMAs aids both dispersion and degradation processes, while the formation of SRBs and SOMs hinders these two

processes. Therefore, OMA formation is considered a natural remediation process. In recent years, remediation engineers have also attempted to develop cost-effective strategies to enhance OMA formation in order to disperse and degrade large quantities of oil (Ajijolaiya et al., 2007). Conversely, remediation engineers are concerned with SRB and SOM formation and have sought ways to safely and efficiently remove these residues from the environment.

2.4.2.1 Remediation methodology for enhancing microscopic aggregate formation

The cost-effectiveness and environmental friendliness of dispersion through OMA formation has led to the desire to facilitate this process through human intervention to speed up oil spill remediation. This is done through two methods: 1) moving contaminated sediment from the high tide zone to the low tide zone to enhance OMA formation in a process known as "surf washing," and 2) applying a sediment slurry directly to an oil slick to enhance OMA formation.

The surf washing method requires the movement of oil-contaminated sediments trapped in the supratidal or high tide zones down into the low tide zone, typically through the use of heavy machinery such as a front-end loader. In this way, the wave action in the surf zone may release the oil from the contaminated sediment into the water column where it will have the opportunity to interact with suspended fine sediments and become dispersed as OMAs. One of the earliest reported surf washing efforts was completed at the Bouchard 155 oil spill site in Tampa Bay, FL in 1993. This application resulted in removing stained oil from the sediment after one to two wave cycles (Owens et al., 1995). Another surf washing study was completed following the Sea Empress oil spill in 1996, where sediment relocation resulted in the removal of the majority of beached oil after four days of treatment. During this study,

OMA formation resulting from the surf washing efforts was verified for the first time, via microscopic analyses (Lee et al., 1997). A pilot-scale study, called the Svalbard trials, utilized experimentally oiled beach plots to test the efficacy of surf washing and to obtain further microscopic observational data for OMA formation (Lee et al., 2003a; Sergy et al., 2003). These studies have demonstrated that surf washing can greatly accelerate natural OMA formation, and can help reduce the amount of residual oil trapped in the shoreline system.

Some studies have suggested that OMA formation can be facilitated by directly applying a fine sediment slurry to an oil slick (Bragg and Yang, 1995; Lee et al., 2011; Silva et al., 2015). A field study to test the efficiency of this technique was carried out on an experimental slick, which was created in the ice-infested waters of the St. Lawrence Estuary (Lee et al., 2011). A slurry of calcite and seawater was directly applied to the slick, and the system was then mixed using a boat propeller. As a result, the oil was rapidly dispersed into the water column, with minimal resurfacing. Additionally, microcosms of field samples from this study showed that over 56% of the dispersed oil degraded within a two-month period, despite low temperatures. Niu et al. (2014) utilized a numerical modeling approach developed by Niu et al. (2011) to do mass balance calculations, and to test alternate scenarios for the field trials that were carried out by Lee et al. (2011). The model results showed that without the addition of calcite slurry, most of the oil would have become trapped under the ice, while the addition of the slurry allowed a significant amount of the oil to be dispersed as OMAs into the water column, while a lesser amount settled to the seabed (Niu et al., 2014). Silva et al. (2015) completed a mesocosm study that simulated a reflective beach

environment to test the effects of the addition of fine clay and silt to a simulated spill. Their data showed that the use of fine sediment was four times more effective for dispersing the oil when compared to sandy sediment. They also observed a 40 % reduction in the average levels of saturated hydrocarbons over a 21-day period. More recently, the application of fine minerals combined with chemical dispersant has been explored, and this has been shown to be a promising remediation approach (Lee et al., 2012; Wang et al., 2013). In a bench-scale study, Wang et al. (2013) treated three different oils with combinations of kaolinite and chemical dispersant in various ratios and found that 70-90% of the oil could be removed from the surface using this method; this was a significant improvement over the use of minerals alone, which removed of 37-55% of oil from the surface at the same mineral to oil ratio. While these studies show promise for the application of sediment slurries to disperse oil slicks, this technique has yet to be used in response to an actual oil spill.

2.4.2.2 Remediation methodologies concerning macroscopic aggregates

Remediation procedures concerning SRBs and SOMs differ greatly from those concerning OMAs. While remediation teams seek to enhance OMA formation, they seek to both prevent SRB and SOM formation, and to remove these residues if they do form. From an economic standpoint, removal of SOMs and SRBs is especially important when they are formed near pristine amenity beaches, since they could greatly impact the local tourism industry (Cirer-Costa, 2015; Clement et al., 2017). Currently, the only methods to prevent the formation of SRBs and SOMs are methods that completely remove the oil from the environment before it reaches the shoreline; since this is often impossible, remediation teams must resort to removing these residues after they have formed.

Contamination of a shoreline by SRBs and SOMs is typically remedied through the use of heavy machinery paired with manual labor. First, visual and aerial inspections may be used to assess surface contamination that needs to be removed, such as beached SRBs and intertidal SOMs, while sediment cores are used to assess subsurface contamination. It is important to use an appropriate core depth that captures the full extent of contamination. For example, Bernabeu et al. (2009) recognized that the commonly used 0.5 m pits were not suitable for recognizing deeply buried residues from the Prestige oil spill, and recommended the use of a modified suction corer instead. Once contamination has been identified, mechanical sifters are commonly used for the purpose of treating large quantities of contaminated beach sand. These machines pass the surface layer of contaminated sediment through a screen within the equipment, where the fine material (sand) passes through to be returned to the beach, while the large contaminants (SRBs and SOM fragments) are retained and transferred to a debris hopper (Owens et al., 2011). Additionally, excavators may be used to remove larger patches of contamination, such as SOMs. These types of machines were used extensively in the clean-up of the Deepwater Horizon oil spill, particularly during the BP cleanup efforts, known as Operation Deep Clean (ODC), which are discussed in depth below (Hayworth and Clement, 2011).

The goal of the ODC efforts was to reduce beached residues which presented a high risk of human exposure, since tourists could be directly exposed to these residues which can be distributed up to 10 to 50 meters away from the shoreline, depending on the tidal cycles and storm events. A majority of these residues were beach-SRBs (Figure 2-9a), which are softer and drier than traditional SRBs. In order to locate beach-SRBs, ODC workers directly cored

the dry beach all the way to the water table using small auger drills. Areas that contained oil were flagged for further deep cleaning. The sand around these regions was directly excavated to an area of about 150 m^2 all the way to a depth of about 2 to 4 m (close to the water table boundary). The excavated sand was then filtered through mechanical sifters; tests on sections of shoreline where these sifters were used showed 80-95% recovery rates from a single pass (Owens et al., 2011). Figure 2-10 shows some excavation and mechanical cleaning operations completed during these efforts. While ODC was indeed effective in treating large volumes of contaminated sand, these mechanical sifters cannot not remove all of the oil contamination (Hayworth and Clement, 2011; OSAT-2, 2011; Owens et al., 2011). An observational study by Hayworth and Clement (2011) indicated that the sifting process removed all of the well-consolidated solid matrix constituents such as shells, marine debris, and chunks of well consolidated oil-sand agglomerates. However, the process also broke apart some of the softer oil-sand agglomerates into smaller fragments which were then mixed with the clean sand passing through the sieve. Over time, SRBs that were not captured in the sifting machines became buried, and other machinery had to be used to till or mix the soil to bring SRBs back to the surface where they can be captured by sifters (Owens et al., 2011). Overall, the ODC efforts proved to be effective at reducing the immediate risk of human exposure to larger fragments of oil, and it also diluted and reduced soil-phase oil concentration levels. The fragmentation of SRBs during the ODC efforts may have also accelerated both biodegradation and photodegradation processes.

Figure 2-10. Sediment contaminated by SRBs from the Deepwater Horizon oil spill being A) excavated and then B) sifted and returned to the beach.

It is important to note that the use of sifting and tilling machines is limited to removing beach-SRBs that are either atop or buried under dry beach sand. Unfortunately, most SRBs and SOMs are formed under several meters of water and are buried under a benthic sediment layer, and these residues are almost impossible to detect (Michel et al., 2013). The difficulty of locating these buried residues makes the remediation of SOMs mostly impractical. They can be mobile and will be periodically buried, exhumed, and/or transported by shoreline processes. Other than by direct aerial observations (which are possible only when SOMs are exposed by natural sediment transport processes), it almost impossible to locate SOMs. Newer methods to identify and remove submerged oil such as sonar or fluorometry have been explored, but are not used to a significant extent (Hansen, 2010, 2013; Hansen et al., 2014). Another possible field method is to look for the deposition patterns of angular SRBs (which are recently fragmented from SOMs) along the waterline to indirectly assess possible SOM locations. When they are found, it is desirable to immediately remove these SOMs, provided they are buried within the reach of a standard long-arm excavator. Figure 2-11a shows a long arm excavator removing sediments suspected to contain a buried SOM about 30 meters away from the waterline. Unfortunately, even if they are identified using aerial

surveys, our current ability to remove these SOMs is limited by the arm length of the excavator (which is about 20 meters), and the water depth at which these long-arm excavators can operate (which is limited to a maximum of about 2 meters of water depth). Therefore, along the Alabama shoreline the SOM excavation operations could typically only be completed up to about 50 to 60 meters away from the waterline. However, shallow sand bars where SOMs could have formed exist all the way up to about 500 meters away from the shoreline, and it is possible that mobile SOMs and SRBs could have moved even further offshore. Therefore, innovative technologies and excavation methods need to be developed to locate and remove SOMs buried in deeper waters far away from the shoreline.

Figure 2-11. A) An excavator removes a submerged oil mat that resulted from the Deepwater Horizon oil spill. B) A team of volunteers collects SRBs along the shoreline.

SRBs that were either formed from the original arrival of mousse, or later formed from fragmented SOMs, can be distributed over a large shoreline area (OSAT-3, 2013). However, it is impossible to recover SRBs when they are in buried within the subtidal zone. After the Deepwater Horizon oil spill event, a considerable amount of SRBs of various sizes were found to be scattered along the beaches, primarily residing in the swash zone, or in the wet beach area about 5 to 10 meters away from the waterline. Interestingly, a large amount of

SRBs are found mostly mixed with various solid marine debris, and they are typically deposited in the same areas where shells are deposited (see Figure 2-12). No mechanical methods are currently available to remove these SRBs from the swash zone. Therefore, in addition to the use of heavy machinery, cleanup crews are often deployed to manually collect these SRBs (Hayworth et al., 2015). Deepwater Horizon oil spill cleanup efforts employed an army of workers who used crab nets to manually collect the SRBs. Figure 2-11b shows a typical BP cleanup crew manually removing SRBs from the Alabama shoreline in February 2013, almost three years after the spill. The effectiveness of this manual cleanup procedure is currently unclear since these types of operations are typically terminated once certain cleanup goals are achieved. However, these goals are ill defined and the remaining residues may continue to wash ashore for years after the spill. For example, the manual cleanup operations for the BP spill ended in June 2013, however the Clement et al. (2017) study pointed out that large amount of SRBs are still actively deposited on Alabama's beaches as of January 2016. The remnant SRB deposition level can have seasonal variations and may become particularly pervasive following large storm events (Hayworth et al., 2015; Plant et al., 2013). Therefore, more studies are needed to fully understand the long-term fate of SOMs and SRBs formed from large spill events such the Deepwater Horizon spill.

Figure 2-12. Surface residual balls (SRBs) indicated by red circles that are deposited with shells on a beach following the Deepwater Horizon oil spill

One of the most important lessons learned from the remediation of the Deepwater Horizon spill was that sunken oil in the form of SRBs and SOMs can lead to long term problems that are difficult to manage. More recently, researchers have published studies that explored methods for intentionally sinking fresh spilled oil. Abkarian et al. (2013) first recommended applying sediment to an oil slick in order to sink the slick as "armoured droplets" which are macroscopic (millimeter-scale) droplets covered in coarse sediment particles. These armoured droplets have an appearance that is similar to that of SRBs, but with fresh oil. Boglaienko and Tansel (2015) found that by applying sediment to fresh crude oil, up to approximately 95% of the oil could become trapped in armoured droplets, which they referred to as "particle-oil aggregates." Follow-up studies on this technique showed that that materials with higher surface porosity and a particle size smaller than 2 mm captured a greater amount of oil (Boglaienko and Tansel, 2016a), and the application of chemical dispersant could partially release the oil trapped in these aggregates (Boglaienko and Tansel, 2016b). They argued that "*sedimentation of floating crude oil to the bottom of water column does not eliminate the toxic compounds from being released to the environment, but reduces*

their mobility (i.e., keeping the impact radius small) and prevents direct contamination of beaches, birds, and coastal flora." (Boglaienko and Tansel, 2016a) However, the ramifications of sinking oil in this way on benthic organisms are unknown. For instance, by sinking oil immediately, you would prevent key weathering processes, such as evaporation and photodegradation, from occurring. These weathering processes are crucial for rapidly removing a significant portion of the oil mass, and preventing them would lead to exposing sediments and the water column to toxic components such as BTEX (benzene, toluene, ethylbenzene, xylenes) and lighter PAHs. Additionally, the US EPA has explicitly banned the use of sinking agents for oil spill remediation according to 40 CFR §§ 300.310(b) and 300.910(e). Therefore, careful consideration should be given to prevent adverse ecological impacts before any attempts are made to intentionally sink oil in nearshore environments.

2.5   Impacts

2.5.1   Human and environmental health impacts caused by microscopic aggregates

Dispersing oil as OMAs has been promoted as a non-toxic alternative to the use of chemical dispersants, which may have potential negative toxic effects (Chapman et al., 2007; Linden, 1975; Ramachandran et al., 2004). However, the formation of microscopic OMAs can result in the transport of oil from surface slicks or contaminated beach sediments into the water column or the benthic zone, both of which host a variety of flora and fauna; therefore, it is important to understand how OMA formation may impact sensitive organisms in these zones. As part of the Svalbard Trials, which verified the efficacy of surf washing as a means for stranded oil removal, tests were carried out to assess the effect of enhanced OMA formation through surf washing on the toxicity levels of beach sediment, nearshore waters,

and nearshore sediment (Lee et al., 2003b). Two sites with naturally different wave conditions were experimentally oiled and treated by surf washing. At the site with higher-wave energy conditions, the toxicity levels in the relocated beach sediment were reduced to background levels within 5-10 days. In contrast, at the site with lower wave-energy conditions, a significant toxicity response was evident in relocated sediment 10 days after treatment, and after 61 days there was little difference between the toxicity levels of surf washing and natural attenuation plots. At both of the surf washing plots, residual oil concentrations in surface sediments were found to increase with increasing distance from the shore, and were higher overall at the site with lower wave energy. These trends are due to reductions in turbulence under calmer conditions and at increasing distances away from the shore. As the mixing energy decreases, OMAs and other fine particles can be expected to settle at higher rates. However, it was concluded that based on the guidelines put forth by the Environment Canada, toxicity levels were not of significant concern at these test sites despite the accumulation of residual oil (Lee et al., 2003b).

The results of the toxicity testing on the Svalbard trials support the generally held assertion that dispersion through OMA formation has a net positive benefit on oil-afflicted nearshore environments. However, no two oil spills are the same, and it is beneficial to examine the potential toxicity of OMAs under a host of different conditions. Numerical modeling efforts have been used to conduct such analyses to explore the potential toxic effects of OMAs to benthic organisms (Niu et al., 2010; Niu et al., 2011). Niu et al. (2011) showed that OMA toxicity to benthic organisms is largely dependent on the type of sediment present. Of four types of sediment used in their hypothetical simulation, only one posed

likely risks to benthic organisms. The type and chemical composition of the oil can also significantly impact toxicity risks. Niu et al. (2010) found that the risks associated with aromatic hydrocarbons were greater than those associated with aliphatic groups; their simulations showed that the overall risks due to toxicity effects decreased as the oil weathered. OMA formation can also present risks to nektonic and planktonic organisms in the water column, although the risk to these organisms is of lesser concern than the risk to benthic organisms (Moreira et al., 2015; Rios et al., 2017).

2.5.2   Human and environmental health impacts caused by macroscopic aggregates

A key factor of oil spill remediation is determining when further remediation, such as the removal of SRBs and SOMs, will do more harm than good to the environment. The risks associated with various forms of un-aggregated macroscopic oil residues (e.g. oil slicks, oil stained sediment, dissolved oil components) in both the water column and sediment have been explored in depth with regards to exposure to humans and various marine species (Barron, 2012; Dupuis and Ucan-Marin, 2015), and microorganisms (Kimes et al., 2014; Kostka et al., 2011; Rodriguez-r et al., 2015); however, the impacts of macroscopic aggregates are not as well understood (Warnock et al., 2015). Unlike fresh oil, the oil that is found in macroscopic aggregates has lost some (albeit, not all) of its toxic compounds due to weathering, and does not present the risks of coating or smothering animals like liquid oil residues do; however, humans and wildlife may still be exposed to SRBs and SOMs through either physical contact or accidental ingestion. Additionally, as long as the aggregate remains intact, the oil is less available to partition to other environmental phases; however, the eventual breakdown of macroscopic aggregates may release the oil into more mobile phases,

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such as sediment, which can increase potential risks. For example, since the Deepwater Horizon oil spill, oil contaminated sediments have been shown to be toxic to several Gulf of Mexico species including killifish (Dubansky et al., 2013) and sheepshead minnows (Raimondo et al., 2015). Based on ingestion or dermal exposure, and the potential to breakdown into more mobile fragments, SRBs and SOMs may pose threats that stem from the presence of toxic oil hydrocarbons, metals, or human pathogens that may remain within these residues for extended periods of time (Dickey and Huettel, 2016).

The OSAT-2 (2011) report took into account the exposure of both humans and wildlife to SRBs almost a year after the Deepwater Horizon spill, as well as the impact of continued remediation efforts on resident species. In this report, it was determined that the potential impact to humans for both short and long-term exposure were below acceptable health-based risk and hazard levels put forth by the US Environmental Protection Agency (USEPA) (OSAT-2, 2011). Additionally, the OSAT-2 report concluded that any further cleanup from that point on would have a greater negative impact on local species than the SRBs and SOMs would have if they were left in place. The greatest risk that remnant SRBs and SOMs posed to the wildlife considered in this report comes from ingestion of SRBs and SRB fragments by shore birds, and from the exposure of sea turtle eggs and hatchlings to buried residues. Further remediation efforts were expected to have significant negative impacts on all species considered except for fish and aquatic invertebrates, with particularly high impacts being expected for avian species (OSAT-2, 2011).

Since the release of the OSAT-2 report, additional studies have shown concerns about the toxicity of SRBs, specifically because of the continued presence of some toxic compounds

including PAHs (John et al., 2016; Lemelle et al., 2014; Yin et al., 2015), environmentally persistent free radicals (EPFRs) (Kiruri et al., 2013), genotoxic and carcinogenic metals (Liu et al., 2012; Wise Jr et al., 2014), oxygenated compounds (Aeppli et al., 2012; Huba and Gardinali, 2016; White et al., 2016), and human pathogens such as *Vibrio vulnificus* (Tao et al., 2011). A recent study on the neurotoxic effects of residues from the Deepwater Horizon spill showed that the water accommodated fraction from SOM fragments can lead to the generation of reactive oxygen species which can negatively impact cell membrane integrity and permeability, or lead to programmed cell death. The study concluded that SRBs and SOMs have the potential to be toxic to epithelial, kidney and neuronal cells (Bhattacharya et al., 2016). Wise Jr et al. (2014) detected nickel and chromium, both known human carcinogens and genotoxicants, at levels of up to 8.5 and 4.8 ppm, respectively, in SRB samples collected from the Florida, Alabama, and Louisiana coasts. Benthic residues collected in the Caribbean Sea and in the Gulf of Mexico (prior to the Deepwater Horizon spill) have been found to contain up to 135 ppm of nickel (Pequegnat and Jeffrey, 1979). These metals have been shown to bioaccumulate in marine animal tissues, but they have poor absorption in mammalian gastrointestinal tracts and across mammalian skin, therefore ingestion and dermal absorption are not likely paths for nickel and chromium to present toxicity (Wise Jr et al., 2014). Kiruri et al. (2013) suggested that EPFRs in large SRBs are not likely to be hazardous because these larger residues are not likely to be inhaled or ingested, but EPFRs on much smaller SRB fragments may pose a risk of cardiopulmonary disease to wildlife species. Tao et al. (2011) suggested that the elevated number of *V. vulnificus* found in SRBs may lead to severe infections if exposed to a wound, and can also

lead to infection in immunocompromised individuals, which could lead to fatality. Increased content of OxHCs that have been found in SRBs (Aeppli et al., 2012; Huba and Gardinali, 2016; White et al., 2016) may also present toxic effects, since their increased hydrophobicity may make them more bioavailable (Charrié-Duhaut et al., 2000).

There have been few studies concerning the environmental effects of SRBs and SOMs prior to the Deepwater Horizon spill, and they have presented some conflicting results (Warnock et al., 2015). Junoy et al. (2013) studied sandy beaches that were affected by SRBs from the Prestige oil spill and concluded that the beached SRBs and other residues had minimal effects on the macroinfaunal communities within the first six months after the oil spill, and had no obvious effects after that. Serrano et al. (2006) surveyed benthic areas affected by macroscopic aggregates following the Prestige oil spill and found that these aggregates had no significant effects on health indicators for benthic communities. Kalke et al. (1982) observed the effects of weathered oil resulting from the IXTOC I oil spill on estuarine benthic communities both in the laboratory and in situ. The oil type and environmental conditions of the IXTOC I spill differed from Deepwater Horizon spill, however the oil residues had similar sand content (90%) to those observed following the Deepwater Horizon spill. While laboratory results showed no significant impacts to benthic organisms, the in situ observations showed a substantial reduction in biomass. In contrast, in situ observations made nine years after the Haven super tanker spill in the Mediterranean Sea showed that areas with significant amounts of SRBs or SOMs had no noticeable effect on the benthic communities nine years after the spill. (Guidetti et al., 2000). However, the lack of observed toxic effects could have been due to the amount of time between the spill and the

observations, or the fact that the spilled oil was combusted before sinking, which would have removed many toxic compounds.

2.6   Discussion

Currently, there is a plethora of published research on the occurrence of OMAs, and a less extensive, but still robust, range of published research on the occurrence of SRBs and SOMs. Based on a review of this literature, we have identified several knowledge gaps, which are discussed below, and further research is recommended to fill these gaps.

2.6.1 Terminology

OMAs, SRBs and SOMs are classified using separate terminology primarily as a result of their various sizes, but there is also a vast difference in how these aggregates are viewed by the oil spill remediation community; therefore, it is important to clearly distinguish them using distinct nomenclature to describe each type of aggregate. Based on a review of the terminology used in previous literature to describe these aggregates, this study recommends the following terminology to be used:

- Oil-mineral aggregate (OMA) – microscopic aggregates (<1 mm) which are formed exclusively with oil and fine sediment

- Oil-particle aggregate (OPA) – microscopic aggregates (<1 mm) which are formed with oil and fine sediment and/or fine organic particulate matter

- Surface residual ball (SRB) – macroscopic aggregates (1 mm – 10 cm) which are formed primarily with weathered oil (usually mousse) and sediment (coarse, fine, or both). They are mostly benthic and may have been formed during initial oiling of a beach, or have broken off of a larger SOM. Occasionally, non-benthic SRBs can

also be formed on dry beaches when beached mousse is covered by dry or partially wet sand.

- Surface residual patty (SRP) – macroscopic aggregates (10 cm – 1 m) which are formed primarily with weathered oil (usually mousse) and sediment (coarse, fine, or both), and is negatively buoyant. SRPs may have been formed during the initial oiling of a beach, or have broken off of a larger SOM.

- Submerged oil mat (SOM) – macroscopic aggregates (>1 m) which are benthic agglomerates formed in the nearshore environment. SOMs are formed primarily with weathered oil (usually mousse) and sediment (coarse, fine, or both).

The authors believe that using common terminologies will facilitate discussions both between researchers studying different sizes of aggregates, as well as between researchers studying different oil spills.

2.6.2 Formation

There have been several observations of the occurrence of both microscopic and macroscopic aggregates forming in the aftermath of oil spills that affect sandy beach environments. Nearshore environments present conditions that are conducive to the formation of both of these aggregates, with the presence of fresh oil and fine sediment being more conducive to OMA formation, while the presence of highly weathered oil and sand is more conducive to SRB and SOM formation. While there are many field observations of SRBs and SOMs, understanding of their formation is limited. In contrast, there is an abundance of work that has been done to understand how numerous variables affect OMA formation. Therefore, it is suggested that the influence of oil, sediment, and environmental

variables on SRB and SOM formation be explored, similar to the research that has been completed for OMAs. Additionally, there is a dearth of studies which examine the formation of both microscopic and macroscopic aggregates simultaneously. In environments where both fine and coarse sediments are present, or in a coarse sediment environment where fine sediment is artificially added to facilitate OMA formation, both could have the potential to form subsequently, or even simultaneously. Since nearshore environments are conducive to the formation of either microscopic or macroscopic aggregates under different conditions, it is recommended that further research be done to explore what conditions are more favorable to each type of aggregate, as well as to understand situations where microscopic and macroscopic aggregates may form simultaneously.

2.6.3 Fate

The formation of OMAs benefits oiled shorelines by dispersing oil, while the formation of SRBs and SOMs traps oil in nearshore environments and can lead to periodic re-oiling of beaches for years after a spill. Additionally, OMAs tend to enhance oil degradation, while SRBs and SOMs inhibit oil degradation. Therefore, researchers seek to enhance OMA formation, while they typically seek to prevent SRB and SOM formation, and remove these aggregates when they do form. It is well documented that the natural presence of fine minerals in a nearshore environment, or the application of sediment slurry directly to an oil slick will enhance OMA formation; however, fine minerals may also stabilize emulsifications, which are more likely to form SRBs and SOMs than unemulsified oils. Additionally, studies on OMA formation do not typically report the characteristics of the undispersed fraction of oil. Therefore, it should be investigated whether or not the natural

incorporation of suspended fine minerals, or the engineered application of sediment slurry to weathered oil may lead to the inadvertent sinking of the undispersed fraction of oil as SRBs/SOMs. Understanding this process can help guide remediation decisions concerning the engineered enhancement of OMA formation, and can help determine the fate of the undispersed fraction of oil when fine and coarse sediments are present simultaneously.

2.6.4 Impacts

Knowledge of the toxicity of both microscopic and macroscopic aggregates is currently limited. Additional in situ and mesocosm studies are recommended to better understand if and how toxic compounds trapped in SRBs and SOMs may partition into the surrounding medium to affect various species, and how OMAs that are formed from a variety of oil and sediment types may affect benthic habitats. Such studies can provide guidance on remediation tactics to ensure that more good than harm is done to the afflicted environment.

2.7 Conclusion

This is the first known effort to synthesize information on both microscopic (OMAs) and macroscopic (SRBs and SOMs) aggregates that form in nearshore environments. Researchers often focus explicitly on only one of these classes of aggregates; however, we believe that by understanding the work done by the other group of researchers, studies on either class of aggregate can be significantly furthered. Additionally, collaboration and understanding between these groups may result in more robust predictions of the fate of oil in nearshore environments, which can lead to more informed remediation decisions.

Chapter 3:
Effects of Weathering on the Dispersion of Crude Oil through
Oil-Mineral Aggregation

3.1   Introduction

When oil is inadvertently spilled in a marine environment, one of the major goals of remediation efforts is to disperse the unrecoverable oil into the water column to enhance various natural degradation processes. Dispersion increases the available surface area of the oil which enhances natural processes such as biodegradation and dissolution that play a significant role in degrading the oil (Prince et al., 2003; Prince et al., 1999). Oil can be naturally dispersed by turbulent currents caused by weather events, such as storms, as was observed following the Exxon Valdez oil spill (Wolfe et al., 1994). When weather conditions are insufficient to maintain sustained dispersion, chemical dispersants are often used to promote oil dispersion. This approach was used in the aftermath of major oil spill events such as the Torrey Canyon, Deepwater Horizon and IXTOC oil spills (Jernelöv and Lindén, 1981; Kujawinski et al., 2011; Ramseur, 2010). However, there are several concerns about the potential negative toxic effects of chemical dispersants (Chapman et al., 2007; Linden, 1975; Ramachandran et al., 2004), hence it would be desirable to find environmentally friendly alternative dispersion methods to minimize their use until they are proven to be non-toxic.

When spilled oil enters the coastal environment, it can be dispersed naturally by interacting with suspended mineral fines to form small (typically <1 mm) aggregates in the

water column (Bragg and Owens, 1995; Fitzpatrick et al., 2015; Lee et al., 1997). In the published literature, these microscopic aggregates are referred to as oil-mineral aggregates (OMA) (Lee et al., 1998). Trapping oil as OMA has been recognized as a method for enhancing oil dispersion, and has long been recognized to play a natural role in the remediation of oiled shorelines (Owens and Lee, 2003). Based on laboratory studies, researchers have postulated that OMA formation must have played a significant role in the natural cleansing of shorelines impacted by the Exxon Valdez spill (Bragg and Owens, 1995; Bragg and Yang, 1995). Field studies later confirmed natural OMA formation following the Sea Empress spill (Lee et al., 1997).

Over the past two decades, researchers have sought to enhance the formation of OMA in order to augment natural remediation following an oil spill (Fitzpatrick et al., 2015). Enhancing OMA formation as a dispersant technology has several benefits which include cost effectiveness, reduction of oil slicks, and enhanced degradation rates of trapped oil (Sun and Zheng, 2009). OMA formation decreases the amount of oil in the surface slick, and it has also been shown to increase both the rate and the extent of microbial biodegradation of oil in the water column (Lee et al., 1996; Weise et al., 1999). In addition to increasing the availability of the oil to microorganisms, OMA formation could also reduce the bioavailability and toxicity of the oil to aquatic organisms in the affected environment (Fitzpatrick et al., 2015). In order to take advantage of the benefits of dispersion through OMA formation, researchers have sought for years to find ways to better understand and engineer this process as a low-cost remediation technique to manage oil spills.

There are two main methods that have been explored for enhancing OMA formation: 1) relocating oil-contaminated sediment and rocks from high tide to low tide zones to facilitate a remediation process commonly known as "surf washing," and 2) applying fine sediment, usually in the form of a slurry, directly to an oil slick to promote dispersion (Sun and Zheng, 2009). The "surf washing" method has been applied several times to various oiled shorelines. In 1993, oiled sediments in high tide zones following the Bouchard B-155 oil spill in Tampa Bay, FL were moved into the surf zone by front end loaders, resulting in cleansed sediment after one to two wave cycles (Owens et al., 1995). A similar relocation process was employed following the *Sea Empress* spill in 1996, where most of the beached oil was removed after four days of treatment. The same study verified formation of OMA during the surf washing process using microscopic observations (Lee et al., 1997). A controlled field study that was part of the Svalbard Shoreline Field Trials was carried out using sediment relocation on an experimentally oiled shoreline, where oil-contaminated sediment and rocks were moved from the high tide zone to the low-tide zone. This study confirmed that natural OMA formation can be significantly accelerated by surf washing, leading to a dramatic reduction in the amount of oil trapped on the experimental beach plots (Lee et al., 2003).

In addition to the "surf washing" method, some studies have suggested that oil spill remediation efforts can be enhanced by directly applying fine sediment to an oil slick to facilitate OMA formation (Bragg and Yang, 1995; Lee et al., 2011; Lee et al., 2012). More recent studies have explored various aspects of this idea in greater depth. Zhang et al. (2010) examined the efficiency of OMA formation with alternative materials such as fly ash and graphite that are not typically expected in a beach environment. Additionally, it has been

found that modifying the surface properties of minerals such as bentonite or kaolinite can increase OMA formation (Chen et al., 2013; Wang et al., 2011; Zhang et al., 2010). Recently, a mesocosm study was carried out to determine the potential effectiveness of applying a slurry of sediment and water to oil contamination in a reflective beach environment; the study reported that over 21 days an average of a 40% reduction in saturated hydrocarbons was achieved (Silva et al., 2015). Lee et al. (2011) tested the sediment application method in a field study by releasing crude oil into the ice-infested St. Lawrence Estuary. Their team applied a slurry of calcite and seawater directly to the slick and then utilized the propellers of their vessel to create enough mixing energy to form OMA. They found that the oil was quickly dispersed by this treatment, with insignificant resurfacing of the oil. Additionally, mesocosm studies on samples from this field trial showed that over 56% of the spilled oil was degraded after two months, despite the low temperatures.

In order to determine the most effective way to enhance OMA formation, and to predict the natural extent of the aggregation, many studies have been carried out to better understand the fundamentals of the OMA formation process (Gong et al., 2014; Sun and Zheng, 2009). Through these studies, the impacts of several environmental variables including salinity, sediment concentration, temperature, mixing energy, sediment type and oil type have been explored (Gong et al., 2014). In addition to the effects of natural environmental factors, the effect of chemical dispersants on OMA formation has also been thoroughly studied (Cai et al., 2017; Guyomarch et al., 2002; Khelifa et al., 2008; Lee et al., 2012; Li et al., 2007; Wang et al., 2013). However, there is currently a gap in our understanding of how the degree of oil weathering will affect the OMA formation process over time (Sun and Zheng, 2009).

Understanding this factor is crucial to extrapolating the results from idealized laboratory experiments, which are typically conducted using fresh oil or a single stage of weathered oil. Quantifying weathering effects on OMA formation will also help improve the capability of mathematical models used to predict the temporal variations in OMA formation, and can help develop guidelines for enhancing OMA formation for the treatment of oil spills. This knowledge can also improve risk assessments for environments where OMA form. For example, Niu et al. (2010) adapted their assessment of the risks of OMA to benthic organisms to account for variations in the chemical composition of weathered oil, but did not adjust the model to account for how the total amount of oil that could be transported to the benthic zone as OMA would change as the oil weathers.

Immediately after a spill, the spilled oil begins to weather at an exponential rate, changing both its chemical and physical properties. First, the viscosity of the oil increases as it weathers, which decreases the ability of the oil to form small droplets (Delvigne and Sweeney, 1988). Additionally, as oil weathers, lighter components (e.g. alkanes, aromatics) are removed, while other heavier components, such as asphaltenes become more concentrated (Oudot et al., 1998). Increases in viscosity and asphaltene content have two major effects on OMA formation: first, oils with higher asphaltene content and viscosity are more likely to form stable emulsions (Bobra, 1991); second, since asphaltenes are amphoteric compounds (Poteau et al., 2005), the increase in asphaltene content due to the concentration effect (Trudel et al., 2010) will make weathered oil increasingly attracted to charged surfaces such as clay particles (Bragg and Yang, 1995; Guyomarch et al., 2002).

Most OMA studies use only fresh oil, or a single weathered stage of an oil, and as a result there are some disagreements in the published literature about whether OMA formation increases or decreases as a result of weathering. Based on literature, we have identified two conflicting research hypotheses. We first hypothesize that increased relative quantities of polar and charged hydrocarbons, such as asphaltenes, found in weathered oil will cause an increase in dispersion through OMA formation by increasing the attractive forces between the oil and the negatively charged mineral surface (Bragg and Yang, 1995; Sørensen et al., 2014; Stoffyn-Egli and Lee, 2002). Bragg and Yang (1995) found that weathered oil from the Exxon Valdez spill formed small OMA more readily than a degassed Alaska North Slope (ANS) oil with low polar content which had a similar viscosity; they used this data to suggest that OMA would form more readily with weathered oil. More recently, Sørensen et al. (2014) tested between four different oils and found that those with significantly greater asphaltene content had a greater propensity to adsorb to suspended particulate matter, and therefore predicted that as crude oil weathered and increased in polar content, its ability to form OMA would increase. Our second hypothesis is that the increased viscosity of weathered oils will decrease the formation of OMA. Payne et al. (2003) postulated that increased viscosity associated with oil weathering will lead to diminished oil droplet dispersion and thus decrease OMA formation over time, although their specific experimental conditions prevented direct observations to support this hypothesis. This hypothesis is supported in part by other studies that compared different types of oils with varying viscosities, which have shown that higher viscosity oils form fewer OMA (Kepkay et al., 2002; Khelifa et al., 2002).

Interestingly, the first hypothesis predicts an increase in OMA formation with weathering, while the second predicts a decrease. The objective of this study is to test these two conflicting hypotheses and quantify how the degree of weathering will affect the amount of oil that can be dispersed as OMA. Of the published OMA studies that have used either artificially or naturally weathered oil (Khelifa et al., 2002; Li et al., 2007; Ma et al., 2008; Omotoso et al., 2002; Payne et al., 2003; Wang et al., 2013), very few have compared OMA formation using weathered oil to OMA formed from that oil's fresh counterpart, and none of these studies have examined multiple stages of weathering for the same oil. In this study, five stages of weathering are examined for three types of oil to evaluate how oil dispersion through OMA formation will change as weathering progresses. The results will serve two major purposes: 1) determine if OMA formation increases or decreases with weathering; and 2) determine, through microscopic analyses, how OMA structure will change with weathering.

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3.2   Methods

3.2.1   Materials

Three types of oil were used in this study: Louisiana Sweet Crude (LSC), Texas Intermediate Crude (TIC), and California Heavy Crude (CHC). LSC oil was supplied by Goodway Refining LLC (Atmore, AL, USA). TIC oil was supplied by Texas Raw Crude

(Midland, TX, USA). CHC oil was supplied by ExxonMobil Corporation (Benicia, CA, USA).

All experiments were performed using kaolinite, which has been identified as one of the most effective natural minerals for formation of OMA (Poirier and Thiel, 1941; Wang et al., 2011; Zhang et al., 2010). Natural kaolinite was purchased from Sigma-Aldrich (St. Louis, MO). Dichloromethane (DCM), sodium chloride (NaCl), and cellulose filter papers were supplied by VWR Scientific (Suwannee, GA).

3.2.1.1 Oil weathering

Each type of oil was weathered for 2, 4, 8, and 32 hours, and these stages will be referred to as W2h, W4h, W8h and W32h, respectively; fresh oil will be referred to as W0h. Oil weathering was simulated by dispensing oil onto glass dishes in thin layers (< 1 cm thick) and placing these dishes outside in direct sunlight (Figure 3-1). The dishes were left stationary other than to periodically redistribute the oil by shaking to ensure even weathering. In order to prevent debris from contaminating the oil, the dishes were placed in shallow boxes covered with glass panels. The sides of the boxes were screened to allow for ventilation, but to prevent debris from entering the box. When the samples were not outside, they were stored in a freezer at -15 °C. The amount of solar radiation that the oil was exposed to while weathering was tracked using data from the local weather station located in Auburn, AL. The outdoor weathering method used was similar to the approach used in one of our previous studies (John et al., 2016).

Based on our experimental design, the outdoor weathered oil underwent both evaporation and photodegradation, two major weathering processes experienced by oil slicks. Our

previous research has shown that the glass plate used for covering the protective box (Figure 1) had a negligible effect on evaporation and photodegradation (John et al., 2016).

Figure 3-1. Experimental methods: Left) outdoor oil weathering method; Right) baffled flask experiments

3.2.1.2 Mass loss of oil

The percent mass loss of each stage of weathered oil was determined by comparing the weight of the plate with the fresh oil on it to the weight of the plate with the weathered oil on it.

3.2.1.3 Viscosity of oil

The viscosity of the fresh and weathered oils was determined using a Brookfield rotational viscometer. All stages of LSC, and TIC-W0h were analyzed using spindle 21 and a small sample adapter. The remaining weathering stages of TIC, and all stages of CHC were analyzed using spindle 7.

3.2.1.4 Asphaltene content of oil

Asphaltene content was determined following a modified method of ASTM D3279-12. Fresh oil (10 g for LSC, 0.5 g for TIC, and 0.1 g for CHC) was carefully weighed into a 250

mL Erlenmeyer flask. Approximately 100 mL of n-hexane was added. The contents were stirred and heated at 40 °C for 20 minutes and then filtered through a cleaned glass fiber filter. The glass fiber filter was then dried at 105 °C for 2 hours and then weighed to determine the asphaltene content in the oils.

Since asphaltenes are conservative compounds and are resistant to weathering (Oudot et al., 1998), the asphaltene content of the weathered oils was estimated based on percent mass loss of oil after weathering using the following formula,

$$ac_f = \frac{ac_o}{(1 - m_{loss})} \qquad (1)$$

where ac_o is the original asphaltene content measured in the lab, ac_f is the final estimated asphaltene content at a given weathering stage, and m_{loss} is the percent mass loss of the oil due to weathering.

3.2.1.5 Mineral characterization

The kaolinite was characterized using a Malvern Mastersizer 3000. D_{50} for the kaolinite was 8.2 μm.

3.2.1.6 Artificial seawater

Artificial seawater (ASW) was produced by dissolving NaCl in deionized water at 3.3 wt% (Sun et al., 2014).

3.2.2 Experimental procedure

3.2.2.1 OMA formation

Experiments were performed following a modified version of the baffled flask test (Venosa and Holder, 2013; Venosa et al., 2002). While commonly used for experiments with

chemical dispersants, baffled flasks have also been used previously for OMA experiments (Lee et al., 2012; Ma et al., 2008; Zhang et al., 2010). Based on preliminary experiments, four replicates of each experiment were performed to measure the total concentration of oil trapped in OMA; a separate replicate was performed and analyzed on a microscope to quantify the size of oil droplets incorporated in the OMA as well as to characterize the different types of OMA formed (Stoffyn-Egli and Lee, 2002).

Three oils were examined (LSC, TIC, and CHC), each at five stages of weathering (W0h, W2h, W4h, W8h and W32h). Each of the weathering stages was tested at a low (100 mg/L) and high (200 mg/L) suspended sediment content (Sun et al., 2010). Experimental conditions are summarized in Table 1.

Table 3-1: Experimental conditions

Parameter	Type/Value
Artificial seawater volume	120 mL
Types of oil used	Louisiana Sweet Crude (LSC) Texas Intermediate Crude (TIC) California Heavy Crude (CHC)
Oil concentration (amount added)	200 mg/L (24 mg)
Weathering stages	Fresh; weathered for 2, 4, 8 and 32 hours
Sediment	Kaolinite
Sediment concentration (amount added)	100 mg/L (12 mg) 200 mg/L (24 mg)
Shaking time	1 hr
Shaking rate	250 RPM
Settling time	>8 hours

Each experiment was done using a baffled flask (VWR Scientific) fitted with a stopcock near the bottom. First, either 12 mg or 24 mg of kaolinite was added dry to the flask for low and high sediment concentration experiments, respectively. The flask was then filled with 120 mL of artificial seawater, sealed with a rubber stopper and mixed on an orbital shaker at 250 rpm for ten minutes to suspend the kaolinite (Wang et al., 2011; Zhang et al., 2010). Next, 24 mg of oil was dispensed directly onto the water surface using a syringe. The weight of oil applied was measured by weighing the syringe before and after the oil was dispensed. The flask containing oil, artificial seawater, and kaolinite was then covered and shaken at 250 rpm on the orbital shaker for one hour, after which OMA formation is assumed to have leveled off at this shaking rate (Sun et al., 2014). Flasks were removed from the shaker and allowed to settle overnight for a minimum of 8 hours, after which negatively buoyant OMA, the dominant form following the settling period, were separated for extraction (Khelifa et al., 2008; Sun et al., 2014; Sun et al., 2010). A vacuum pump was used to remove the topmost portion of the flask, leaving behind approximately 20 mL of artificial seawater and negatively buoyant OMAs in the flask (Khelifa et al., 2008). The remaining contents of the flask were transferred directly to a separatory funnel for extraction.

3.2.2.2 Extraction

Extraction was done following a modified version of the extraction protocol outlined by Khelifa et al. (2008). The remaining suspension of kaolinite and OMA was transferred to a 50 mL separatory funnel. DCM was added for each of three consecutive extractions so that the DCM to water ratio was 1:2 for the first extraction, and 1:5 for each of two additional extractions. The extracts were combined and run through a Whatman cellulose filter with a

pore size of 0.45 µm. The filtered extract was blown down under a gentle stream of nitrogen gas, reconstituted to a total volume of 10 mL with DCM, and stored at 4°C until analysis.

3.2.2.3 Analysis – quantifying oil trapping efficiency using spectrophotometry

The concentration of oil captured in the negatively buoyant OMA was determined through analysis with a SpectraMax M2 spectrophotometer (Molecular Devices) using a modified version of the method outlined in Venosa and Holder (2013). Calibration standards were produced by adding a known quantity of oil (25, 50, 125, 250, 375, and 625 mg) to a vial containing approximately 22 mL ASW and approximately 24 mg kaolinite, and then extracting this suspension using the same procedure outlined in Section 3.2.2.2. The calibration standards and experimental extracts were analyzed on the spectrophotometer at wavelengths of 340, 370 and 400 nm. Extracts which were too concentrated to be read on the instrument were diluted as needed, and the formulas were corrected for the dilution.

The area under the absorbance vs. wavelength curve between 340 and 400 nm was determined using the trapezoidal rule with equation 2:

$$Area = \frac{(Abs_{340} + Abs_{370}) \times 30}{2} + \frac{(Abs_{370} + Abs_{400}) \times 30}{2} \qquad (2)$$

The response data for the calibration standards were used to generate a calibration curve, which was then used to determine the concentration of extracts from experiments. Oil trapping efficiency was determined using the following formulas:

$$mass_{OMA} = \frac{Area - b}{m} \times V_{extract} \qquad (3)$$

where $mass_{OMA}$ is the mass of oil in the negatively buoyant OMA, m and b are the y-intercept and slope of the calibration curve respectively, and $V_{extract}$ is the volume of the extract, and

$$OTE(\%) = \frac{mass_{OMA}}{mass_{oil}} \qquad (4)$$

where *OTE* is the oil trapping efficiency, which is the ratio of the mass of oil trapped in OMA ($mass_{OMA}$) to the total mass of oil originally introduced in the experiment ($mass_{oil}$).

3.2.2.4 Analysis – UV-epifluorescence microscopy

One replicate of each experiment was used to analyze the structure of the OMA formed based on the structures identified in Stoffyn-Egli and Lee (2002) (i.e. single droplet, multiple droplet, solid, and flake OMA), including the size of oil droplets incorporated in the OMA. These replicates were run separately from the replicates analyzed for total oil concentration; therefore, an additional replicate was performed, extracted and measured with this set to ensure that results were consistent between trials. The suspension of negatively buoyant OMAs from each microscopy replicate was brought to a total volume of 22 mL with ASW; 10 µL of this suspension was dispensed onto a glass slide. The wet mount was analyzed using a microscope (Advanced Microscopic Group AMAFD1000) with both fluorescent and brightfield microscopy modes. Using fluorescence only, images of 30-40 consecutive fields of view were taken of each slide (Sun et al., 2014). These images were analyzed using ImageJ software (NIH) to measure oil droplet diameter (Rasband, 2016). OMA structures were identified by generating an overlay of the fluorescent image and the transmitted light image so that both oil and sediment could be observed in the same field of view.

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3.2.3 Data analysis

The oil trapping efficiency data was statistically analyzed using Welch's t-test and Pearson correlation. The statistical analysis was done using RStudio (R version 3.2.2).

3.3 Results

3.3.1 Oil properties

3.3.1.1 Fresh oils

The three oils used in this study were selected for their range of oil types, fresh viscosity values and asphaltene contents. LSC had the lowest viscosity and asphaltene content, followed by TIC, and CHC had the highest viscosity and asphaltene content (Figure 3-2).

3.3.1.2 Weathered oils

The viscosity, asphaltene content, and percent mass loss were measured for each stage of weathered oil. Solar radiation was tracked to ensure that samples which were not weathered simultaneously were exposed to comparable levels of solar radiation. The solar radiation exposure, viscosity, asphaltene content and mass loss for each weathering stage of oil are shown in Figure 3-2. The asphaltene content for the weathered oils was estimated from measurements done with fresh oils and the percent mass loss. This is due to the formation of polar constituents during the weathering process which are insoluble in hexane and therefore cause an overestimation of asphaltene content (Oudot et al., 1998). The high resistance of asphaltenes to evaporation and photodegradation for the given exposure time, makes this a reasonable estimation.
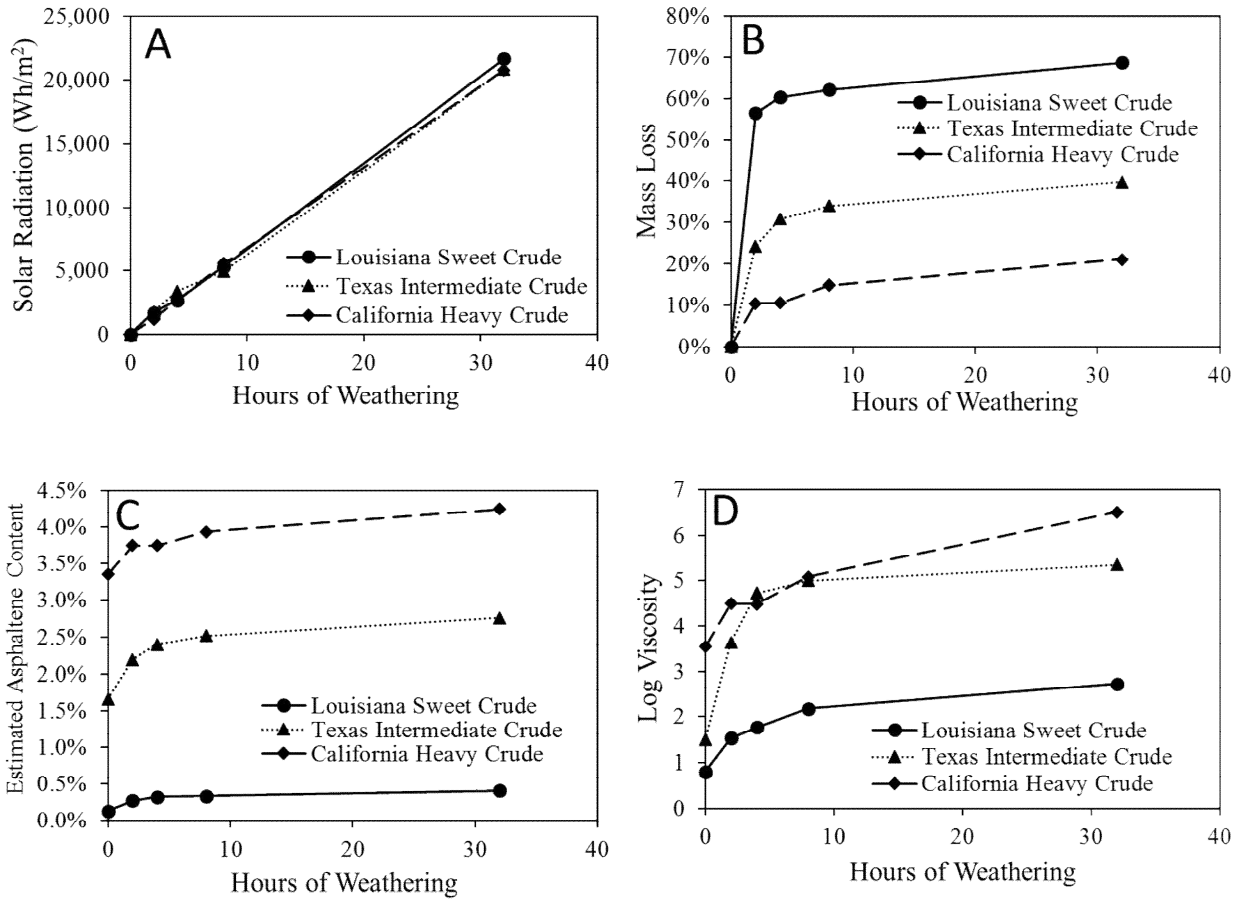
Figure 3-2. A) Cumulative amount of solar radiation; B) percent mass loss due to weathering; C) increases in asphaltene content due to weathering; and D) increases in viscosity (in log scale) due to weathering

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3.3.2 Oil trapping efficiency

The overall capability of an oil to form OMA was quantified as an oil trapping efficiency, which was derived from the spectrophotometric data by computing the fraction of total oil trapped as negatively buoyant OMA with reference to the total amount of oil originally introduced into the system. The oil trapping efficiencies for LSC, TIC and CHC as they weathered over time are summarized in Figure 3-3.
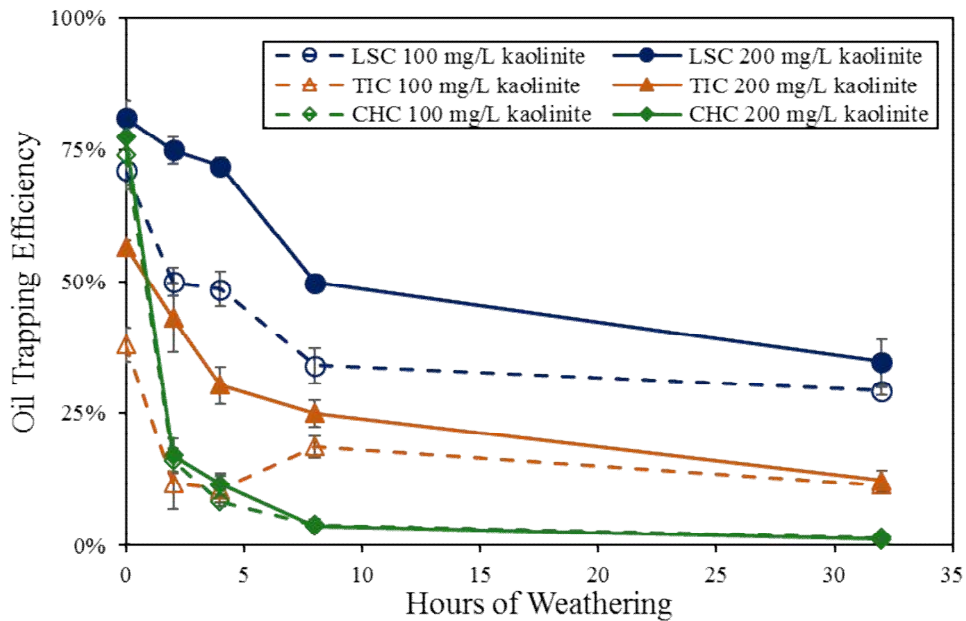
Figure 3-3. Oil trapping efficiency at various weathering levels for Louisiana Sweet Crude (LSC), Texas Intermediate Crude (TIC), and California Heavy Crude (CHC). Open symbols with dotted lines indicate values at low sediment concentrations and filled symbols with continuous lines indicate values at high sediment concentrations.

For LSC, the oil trapping efficiency decreases as the oil weathers. The oil trapping efficiency at the low sediment concentration is significantly lower (Welch t-test, $p < 0.05$) than at the high sediment concentration for all weathering stages except for LSC-W32h for which the efficiency is statistically similar ($p > 0.05$) between low and high sediment

concentration experiments. The more efficient trapping for the higher sediment concentration agrees with the previous findings reported by other studies (Ajijolaiya et al., 2006; Khelifa et al., 2007; Khelifa et al., 2008; Sun et al., 2010). The oil trapping efficiency for low and high sediment concentration, respectively, decreases from 71% and 81% for LSC-W0h, to 29% and 35% for LSC-W32h. Preliminary experiments with sediment concentrations higher than 200 mg/L were conducted, and the oil trapping efficiency was not significantly higher ($p <$ 0.05) than experiments performed with a sediment concentration of 200 mg/L.

Similar to LSC, for TIC the oil trapping efficiency decreases as the oil weathers and is significantly lower for the low sediment concentration for all weathering stages except for TIC-W32h, for which the oil trapping efficiency at the two sediment concentrations is statistically similar. The oil trapping efficiency for low and high sediment concentration, respectively, decreases from 38% and 57% for TIC-W0h, to 11% and 12% for TIC-W32h.

For CHC, the oil trapping efficiency is statistically similar for low and high sediment concentration experiments at all weathering stages except for CHC-W4h, for which the trapping efficiency is significantly lower for the low sediment concentration. The oil trapping efficiency for low and high sediment concentration, respectively, decreases from 77% and 74% for CHC-W0h, to 1% at both sediment concentrations for CHC-W32h.

The correlations of oil trapping efficiency with asphaltene content and oil trapping efficiency with viscosity were tested using Pearson's correlation. The oil trapping efficiency for all three oils has a high negative correlation (>0.75) with asphaltene content. The correlation of oil trapping efficiency with viscosity decreases as the original viscosity of the oil increases. For LSC, the lightest of the oils, oil trapping efficiency and viscosity have a

high negative correlation (0.76); for TIC, the intermediate oil, there is a slightly lower correlation (0.61); and for CHC, the heaviest of the oils, oil trapping efficiency and viscosity have the lowest correlation (0.38).

3.3.3 OMA structure

3.3.3.1 OMA morphology

Observed OMA were classified based on the types of OMA identified by Stoffyn-Egli and Lee (2002). Single droplet OMA consist of a single spherical droplet of oil surrounded by sediment particles; multiple droplet OMA contain several spherical oil droplets stabilized by sediment particles; and solid OMA are irregularly shaped aggregations of oil and mineral particles where individual droplets are not distinguishable. Flake OMA, which appear as membranes, were not observed in any of the experiments in this study.

Single droplet and multiple droplet OMA made up the entirety of LSC-W0h, LSC-W2h, and LSC-W4h OMA observed (Figure 3-4a), and were the numerically predominant form of OMA formed from LSC-W8h and LSC-W32h oils. A small number of the OMA formed from LSC-W8h and LSC-W32h were in the form of solid OMA (Figure 3-4b). Solid OMA have previously been found on the scale of tens of microns, sometimes reaching up to 300 μm (Gong et al., 2014; Stoffyn-Egli and Lee, 2002). The observed solid OMA formed from LSC-W8h oil typically fell in this range; however, solid OMA formed from LSC-W32h oil were found that approached 1 mm in length, more than triple the size of previously observed solid OMA. These large solid OMA approach the upper limit of the size of aggregates that are commonly referred to as OMA (Fitzpatrick et al., 2015). Only single and multiple droplet OMA were observed to have been formed for all stages of TIC (Figure 3-5). The droplets

incorporated into these OMA tended to be relatively uniform in size, with diameters typically ranging from 1-20 μm throughout all weathering stages. A small number of larger droplets were found with diameters up to 85 μm.

The vast majority of OMA formed from CHC were single droplet OMA; multiple droplet OMA were also present, albeit far less common. Extremely large single droplet OMA (100-500 μm diameter), which were visible to the naked eye, were also present in OMA formed with all stages of the oil (Figure 3-6). These extremely large droplets are likely a result of the high viscosity of CHC throughout all weathering stages.

Figure 3-4. Top) Image taken at 20× magnification showing single and multiple droplet OMA with droplets ranging in size from 1 to 20 μm formed from fresh Louisiana Sweet Crude; Bottom) image taken at 10× magnification showing a large solid OMA (≈ 500 μm), as well some small droplet OMA which were formed with 32-hour weathered Louisiana Sweet Crude.
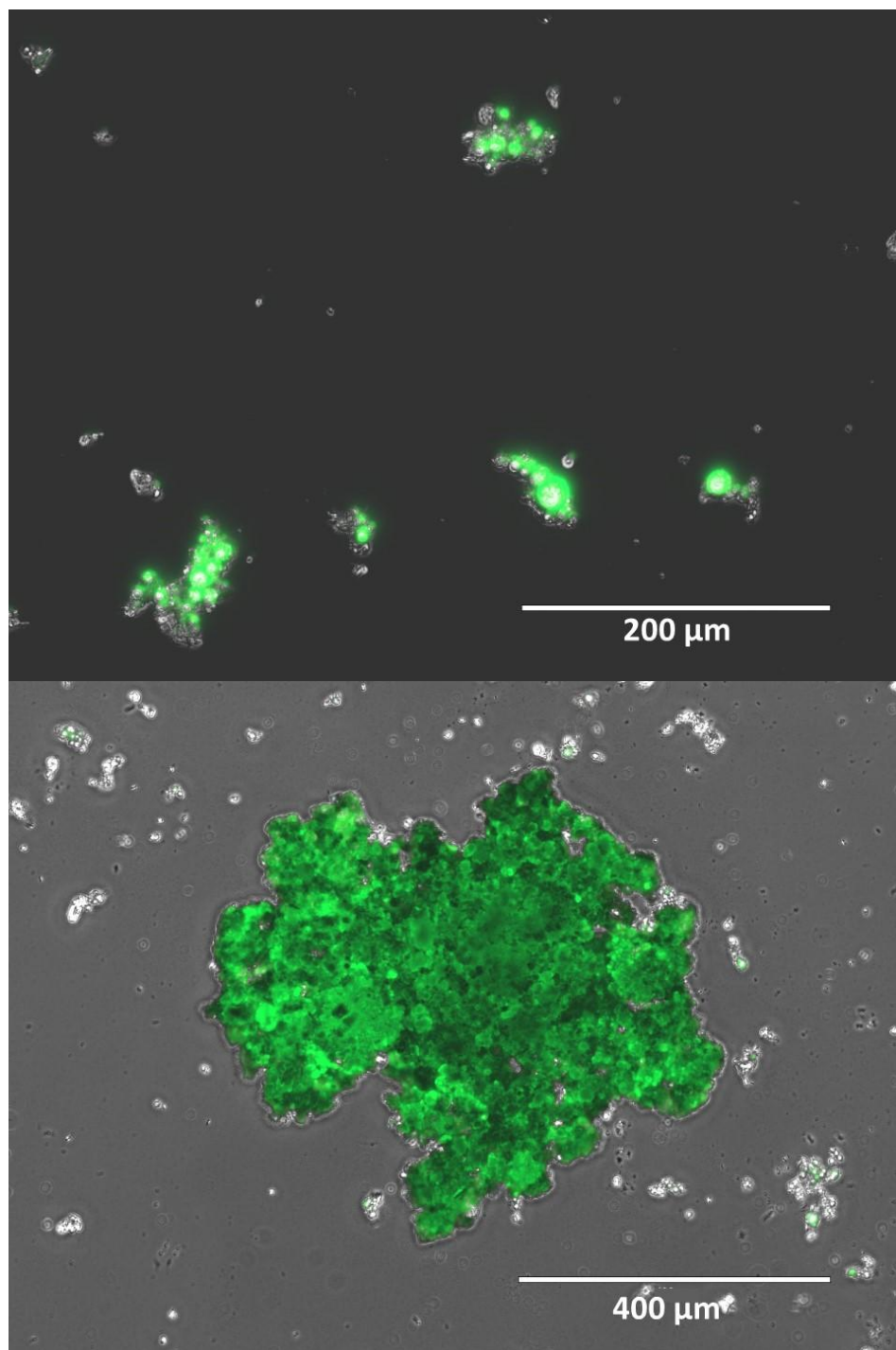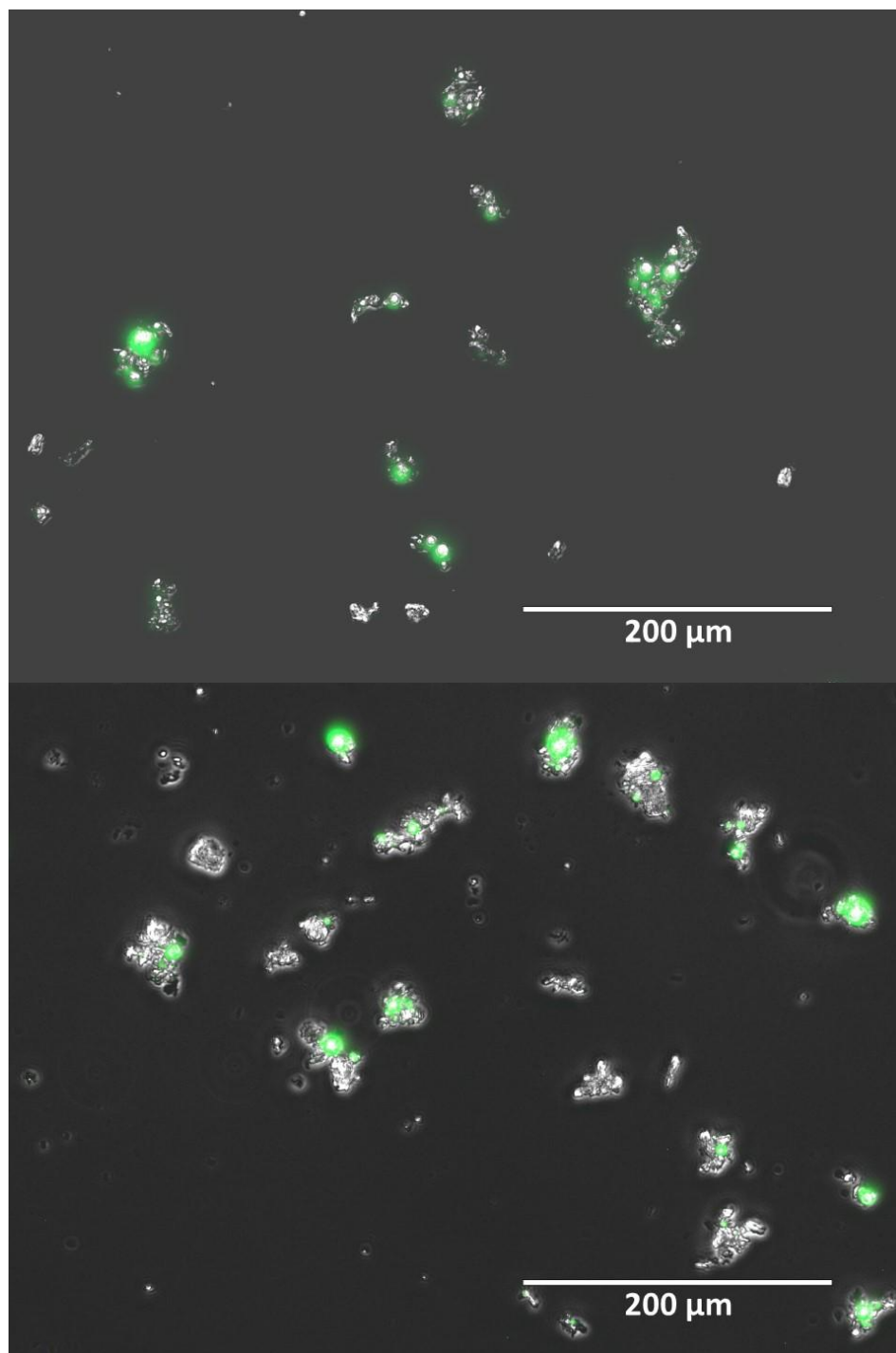
Figure 3-5. Top) Image showing single and multiple droplet OMA with droplets ranging in size from 1 to 20 µm formed with fresh Texas Intermediate Crude; Bottom) image showing single and multiple droplet OMAs formed with 32-hour weathered Texas Intermediate Crude. Both images were taken at 20× magnification.
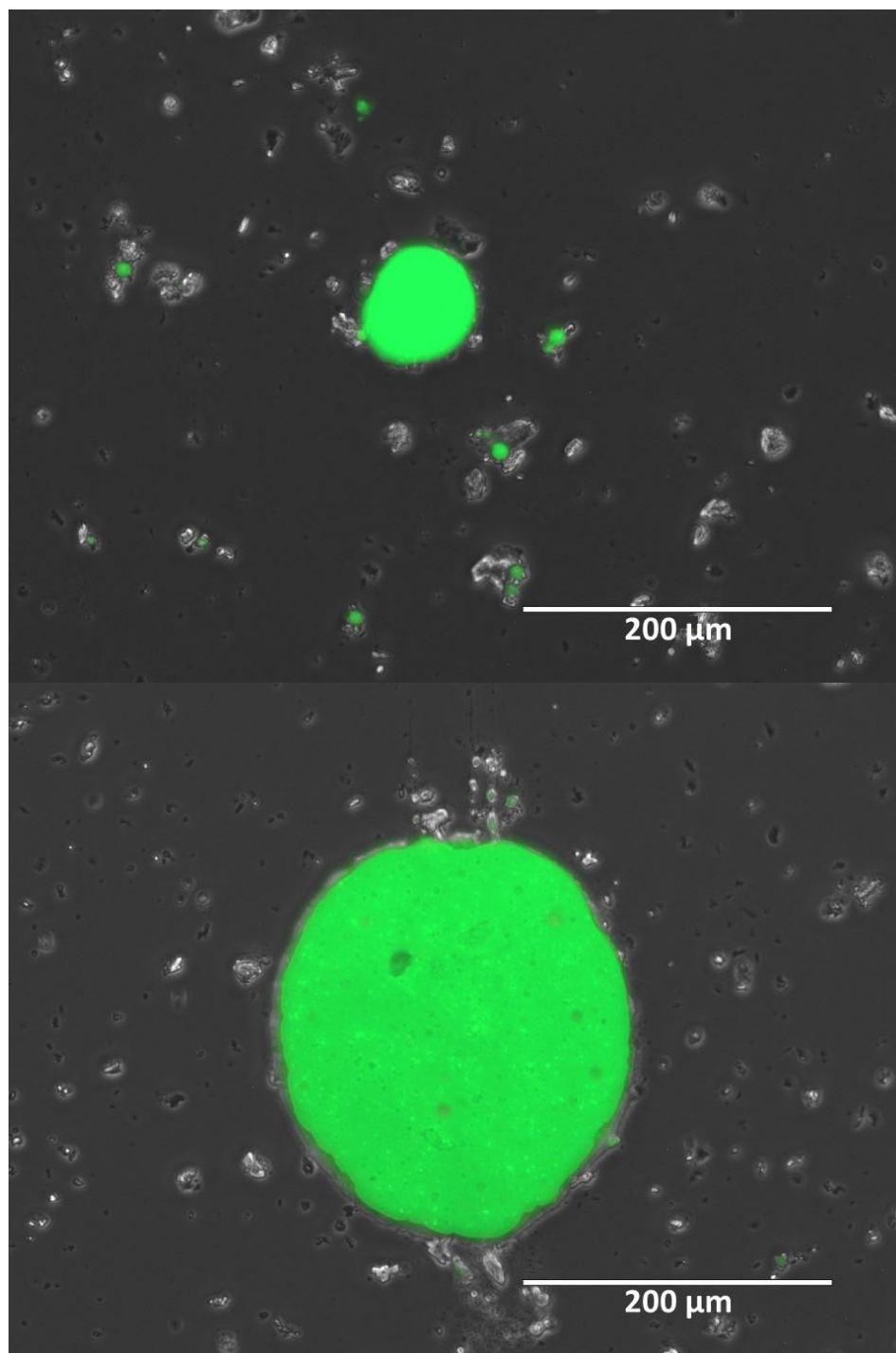
Figure 3-6. Top) Image showing single droplet OMA with droplets ranging in size from 10 to 50 μm formed from fresh California Heavy Crude; Bottom) image showing a large single droplet OMA with a droplet approximately 250 μm in diameter formed from 32-hour California Heavy Crude. Both images were taken at 20× magnification.

3.3.3.2 Droplet size distribution

The size distributions of droplets in OMA formed from each oil are shown in Figure 3-7. The figure shows the percent droplet size smaller than the corresponding values indicated on the x-axis. The average droplet sizes and the droplet size ranges measured in droplet OMA for different oils are summarized in Table 3-2. The diameter of droplets incorporated into single or multiple droplet OMA was measured for all oil types and weathering stages. Only oil droplets that could be distinctly identified as an individual droplet were measured; therefore, a large amount of droplets incorporated into multiple droplet OMA were not quantified.

For LSC, the size of droplets incorporated in OMA increased with weathering. For example, in high sediment concentration experiments the observed droplet size ranged from 1.2 to 28.8 μm for LSC-W0h and from 1.6 to 37.9 μm for LSC-W32H. The average droplet size was 5 ± 3 μm (622 droplets counted) and 9 ± 5 μm (1181 droplets counted) at high sediment concentration for LSC-W0h and LSC-W32h respectively. Both the average and the maximum observed droplet size increased from LSC-W0h to LSC-W32h (Table 3).

For TIC, the size of oil droplets incorporated in OMA decreased with weathering. For example, in low sediment concentration experiments the observed droplet size ranged from 1.8 to 34.2 μm for TIC-W0h and from 1.5 to 31.3 μm for TIC-W32h. The average droplet size was 8 ± 5 μm (464 droplets counted) and 5 ± 4 μm (426 droplets counted) at low sediment concentration for TIC-W0h and TIC-W32h, respectively. The average droplet size

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decreased from TIC-W0h to TIC-W32h samples. There was no clear trend in the maximum droplet size observed from TIC-W0h to TIC-W32h.

Similar to TIC, the droplet size of CHC oil incorporated in OMA decreased with weathering. For low sediment concentration experiments with CHC, the observed droplet size ranged from 0.9 to 90.3 μm for CHC-W0h and from 0.6 to 147.4 μm for CHC-W32h. The average droplet size was 5 ± 8 μm (306 droplets counted) and 2 ± 6 μm (531 droplets counted) at low sediment concentration for CHC-W0h and CHC-W32h, respectively. The average droplet size decreased from CHC-W0h to CHC-W32h samples, while the maximum droplet size observed increased.
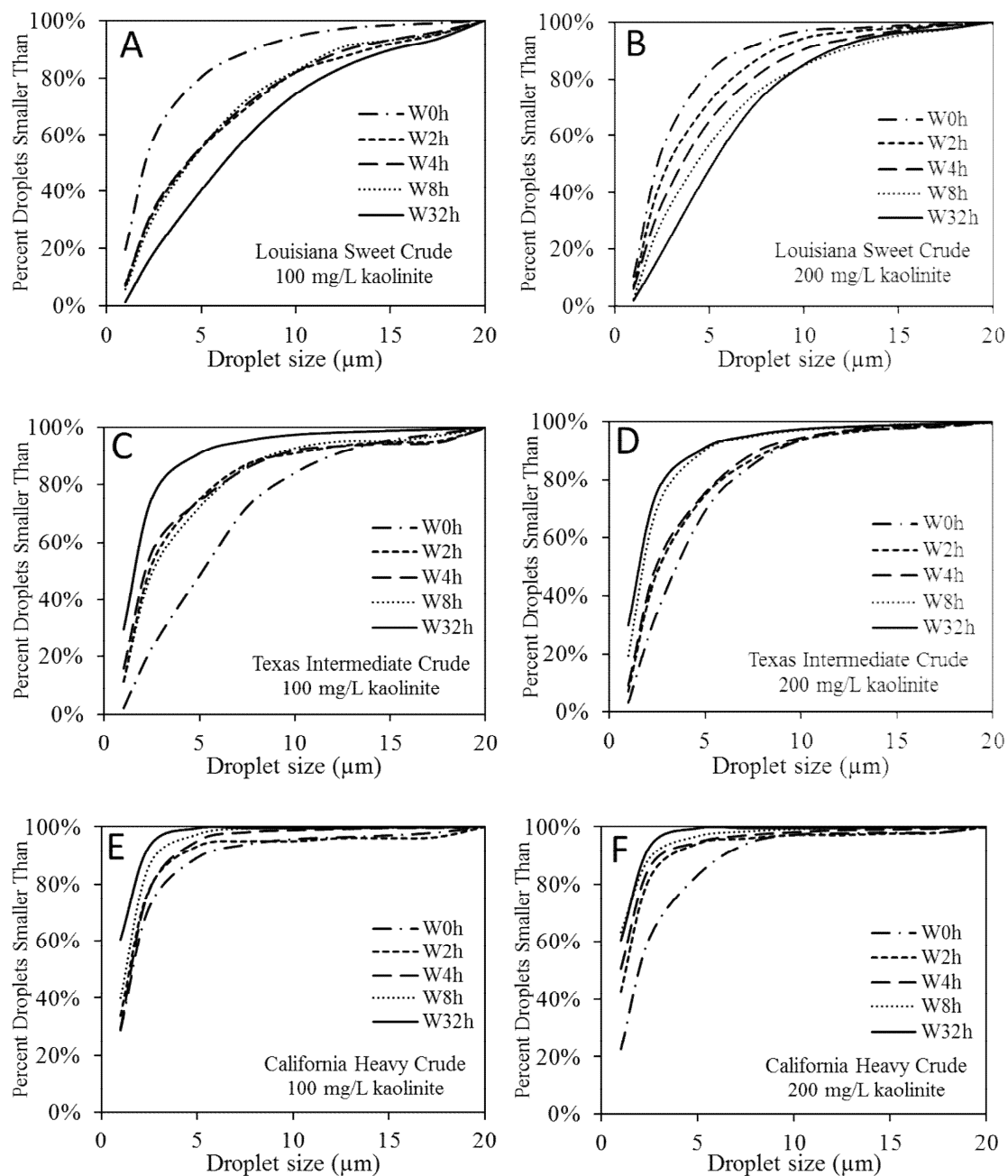
Figure 3-7. Cumulative size distribution of droplets incorporated into single and multiple droplet OMA formed from Louisiana Sweet Crude at low (A) and high (B) sediment concentrations; Texas Intermediate Crude at low (C) and high (D) sediment concentrations; and California Heavy Crude at low (E) and high (F) sediment concentrations.

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Table 3-2: Droplet sizes observed in oil mineral aggregates formed with Louisiana Sweet Crude (LSC), Texas Intermediate Crude (TIC) and California Heavy Crude (CHC) oils. W0h represents fresh oil, and W2h, W4h, W8h and W32h represent oil that is weathered for 2, 4, 8 and 32 hours respectively.

Droplet size (μm)

Oil	W0h Sediment Content Low Mean	Low Range	High Mean	High Range	W2h Sediment Content Low Mean	Low Range	High Mean	High Range	W4h Sediment content Low Mean	Low Range	High Mean	High Range	W8h Sediment Content Low Mean	Low Range	High Mean	High Range	W32h Sediment Content Low Mean	Low Range	High Mean	High Range
LSC	5 ± 4	0.65 – 43.44	5 ± 3	1.19 – 28.83	8 ± 6	0.91 – 54.10	6 ± 4	1.21 – 32.45	8 ± 5	0.97 – 40.02	7 ± 4	1.22 – 29.52	8 ± 5	0.65 – 45.11	8 ± 5	1.72 – 44.28	10 ± 6	1.93 – 63.07	9 ± 4	1.63 – 37.92
TIC	8 ± 5	1.77 – 34.16	7 ± 3	1.40 – 26.31	7 ± 7	1.16 – 56.31	6 ± 4	1.21 – 31.99	7 ± 9	1.29 – 85.24	6 ± 5	1.29 – 69.60	6 ± 5	1.61 - 42.76	5 ± 4	1.05 – 76.46	5 ± 4	1.46 – 31.25	4 ± 3	0.73 – 36.38
CHC	5 ± 8	0.86 – 90.5	5 ± 6	0.93 – 79.12	5 ± 8	0.82 – 86.40	4 ± 7	0.57 – 107.08	4 ± 5	0.85 – 69.13	4 ± 7	0.64 – 150.86	4 ± 7	0.86 – 125.49	3 ± 2	0.76 – 26.63	2 ± 6	0.64 – 147.43	3 ± 12	0.81 – 227.84

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3.4 Discussion

3.4.1 Effects of weathering on OMA formation

Weathering of crude oil in the natural environment greatly alters the oil's chemical composition. As oil weathers, the lighter compounds leave the system, and the concentration of heavier compounds, including asphaltenes, increases due to the concentration effect (Figure 2c). Asphaltenes are charged molecules, therefore as their concentration increases in the weathered oil, the oil's ability to attract clay particles increases. Additionally, when oil undergoes photodegradation a wide variety of daughter products are produced, including polar compounds, which should further increase the attraction of the oil to charged surfaces such as clay particles. Increased polar fractions and asphaltene content may help facilitate the OMA formation process to some degree, however, the clear decrease in oil trapping efficiency as each of the three oils weathered disproves our first hypothesis that OMA formation will increase as oil weathers due to an increased charge in the oil. Contrary to the suggestions of other studies (Bragg and Yang, 1995; Sørensen et al., 2014; Stoffyn-Egli and Lee, 2002), our study shows no evidence that increased ratios of polar and charged components in oil will overcome the detrimental effects that other weathering-induced physical and chemical changes will have on OMA formation. Lower molecular weight polar compounds which are water-soluble (Lee, 2003) may leave the spilled oil system due to their higher solubility, which might explain, in part, why the polar fraction does not play a more significant role in enhancing OMA formation.

The physical properties of oil are also altered through weathering; most notably the viscosity of oil increased significantly as it weathered (Figure 2d). The results of this study

indicate that the amount of oil that can be dispersed as OMA is highest immediately following a spill, when the oil is still fresh and has the lowest viscosity. At later times, the amount of oil incorporated into OMA will continuously decline as the oil is exposed to the environment. These results support our hypothesis that the increased viscosity of weathered oils will decrease the oil's ability to disperse through formation of OMA. This is consistent with the suggestion of Payne et al. (2003) that drastic increases in viscosity due to weathering will cause OMA formation to diminish in the days following a spill.

The results of this study show that despite increases in polar and charged compounds, the drastic increase in viscosity over time results in a net decrease in dispersion through OMA formation as oil weathers. Payne et al. (2003) suggested that increased weathering would cause OMA formation to be limited to 24-48 hours after a spill, except in cases of extremely high turbidity from severe storms or large waves in the nearshore environment. However, the relatively successful trapping efficiency of LSC-W32h, which is representative of a light crude oil weathered for approximately four sunny days (8 hours of intense sunlight per day) suggests that for lighter oils, OMA formation may continue for a more extended period of time following a spill. This was not the case with TIC or CHC, which had oil trapping efficiencies of only around 10% and 1% respectively for W32h oil; therefore, after several days of weathering, dispersion through OMA formation should be considered to have minimal impact on spills of these heavier oils.

3.4.2 Effects of weathering on OMA structure

The decreasing ability of an oil to disperse as small droplets as viscosity increases is a well understood concept (Delvigne and Sweeney, 1988). As oil weathers, the viscosity

increases, leading to the formation of larger droplets. This trend is evident in observations of LSC oil droplets trapped in OMA (Figure 7 a and b). These larger droplets result in a decrease in surface area, and therefore a decrease in interactions between clay and oil resulting in reduced oil trapping efficiency.

Observations of TIC and CHC oil droplets in OMA demonstrates a trend contrary to that shown for LSC. For both TIC and CHC, the size of observed droplets decreases with increased weathering (Figure 7 c, d, e and f). Sun et al. (2014) suggested that suspended particulate matter may decrease the diameter of dispersed oil droplets. These results indicate that this may be increasingly true for more weathered stages of intermediate and heavy crude oils.

3.5   Implications

This study demonstrates that OMA formation will decrease as crude oil weathers, irrespective of the original viscosity and asphaltene content for the types of oil examined here. Since the open ocean typically has very little suspended particulate matter, natural OMA formation should have little to no effect on the dispersion of the oil while it remains far from the shore. Therefore, the proximity of a spill to the shoreline, and consequently the amount of time that an oil can weather as it is transported, can have a drastic effect on how the oil is naturally dispersed through OMA formation. Results from LSC show that for a light crude oil, significant amounts of oil can be dispersed as OMA, even days after a spill; however, results from TIC and CHC indicate that the amount of oil that can be dispersed as OMA will be significantly limited for intermediate and heavy crude oils after only a day or two of weathering, compared to dispersion when they are fresh. While dispersing oil through

facilitating OMA formation may not be more effective than using chemical dispersants in environments that are favorable to oil weathering, it could be the only prudent alternative when the use of chemical dispersants is undesirable or prohibited, such when an oil spill affects a highly sensitive coastal environment that supports diverse flora and fauna.

Microscopic analysis showed that weathering altered the type of OMA formed only for LSC. Otherwise, the type of OMA formed and the size of the droplets incorporated in OMA stayed relatively consistent throughout the weathering stages; only the total amount of dispersed oil differed. This could have implications on the bioavailability of the oil that is captured within OMA. Based on available surface area alone, the bioavailability for TIC and CHC would not be expected to change significantly, although the bioavailability of LSC trapped in OMA might decrease with weathering as solid OMA become more dominant. However, the composition of the weathered oil differs from that of fresh oil, which will also inevitably affect the degradation of the oil (Clement et al., 2017; Yin et al., 2015). Further studies are needed to quantify the degree to which the various degradation processes differ for OMA formed from oil at various stages of weathering.

Field trials are needed to gain a more comprehensive understanding of how weathering affects OMA formation as a result of weathering processes such as emulsification, dissolution and biodegradation (which were not simulated in this study), and additional external environmental parameters (e.g. sunny vs cloudy, or hot vs cold). Better understanding of these environmental effects could help develop improved mathematical models for predicting natural OMA formation, as well as useful guidelines for promoting engineered enhancement of OMA formation as an oil spill remediation method.

Chapter 4:
Conclusions, Limitations and Recommendations

4.1   Summary

This work presented a comprehensive review of the various aggregates that can form when oil and minerals interact in nearshore environments. A key contribution of this review is the recommendation of uniform nomenclature to refer to these aggregates in future studies. The utilization of a uniform nomenclature should facilitate discussions and collaborations between researchers that focus exclusively on either microscopic (OMAs) or macroscopic (SRBs or SOMs) aggregates. This review also extensively explored the current state of knowledge regarding the formation, fate and impacts of these aggregates in nearshore environments. The effects of environmental conditions, oil type, and sediment properties on OMA formation are well understood, but data on the influence of these parameters on the formation of SRBs and SOMs is poorly understood. The formation of OMAs benefits the environment by dispersing oil and enhancing biodegradation; conversely, the formation of SRBs and SOMs is detrimental to the environment because they can severely retard oil weathering processes and result in the re-oiling of beaches for years following a spill. Therefore, researchers have sought ways to engineer enhanced OMA formation, and deter and remediate SRB and SOM contamination. The formation of OMAs is thought to have a net positive impact on the health of nearshore ecosystems; however, OMAs still present some level of risk to benthic communities. The formation of SRBs is thought to have a net negative impact on the health of nearshore ecosystems, and may also pose a toxicity threat to humans.

However, these risks are mostly theoretical, and actual data on the impact of SRBs and SOMs on nearshore species and humans is limited.

One of the key knowledge gaps identified by this review was the lack of understanding of how weathered oil impacts the formation of microscopic OMAs. Prior to the Gustitus et al (2017) study (Chapter 3 of this thesis), there were two conflicting hypotheses regarding this process in the literature. The first hypothesis was that as oil weathers, the increased viscosity of the oil would cause a decrease in OMA formation. The second hypothesis was that as oil weathers, the increased polarity of the oil would cause an increase in OMA formation. Based on the experimental results presented in Chapter 3, it is clear that as oil weathers, OMA formation will decrease. Therefore, it can be assumed that the physical changes that result from oil weathering influence OMA formation more than the chemical changes that result from oil weathering.

4.2   Limitations

The bench-scale study presented in Chapter 3 was intended to represent an idealized environment, therefore artificial seawater was used instead of natural seawater. The use of artificial seawater excluded microbes and organic matter that are present in natural seawater. In natural systems, oil may aggregate with material or biological origin such as bacteria, phytoplankton, dead cells or extracellular polymers, to form marine oil snow. Therefore, in a natural environment the presence of organic matter would have affected the oil trapping efficiency value, most likely by increasing it, however this was not examined here.

In our study, we produced artificial seawater similar to approaches used by previous OMA studies (Chen et al, 2013; Khelifa et al, 2008; Sun et al, 2010; Zhang et al, 2010). The pH of the artificial seawater could have varied between experiments since the water lacked any buffers to stabilize the pH. Interestingly, none of the other studies that used artificial seawater have focused on the effects of pH, which could have played a role in controlling the surface charge of the minerals and hence the aggregation process. However, based on the data from many replicates performed for each experiment within our own study, we believe that pH variation would not have had a significant effect on OMA formation. We recommend that future studies investigate the effects of pH on the aggregation of oil with fine minerals.

4.3 Recommendations for future research

Several recommendations for broad topics that should be researched in greater depth are presented in Chapter 2. The influence of oil type, environmental conditions, and sediment properties should be studied in greater depth for the formation of SRBs and SOMs, just as they have been for OMAs. Research in this area could provide insight for predictions of when either microscopic or macroscopic aggregates will dominate in nearshore environments that are affected by oil spills. Additionally, there is currently only a shallow understanding of the toxic impacts that either microscopic or macroscopic aggregates may have. Therefore, it is recommended that in-situ studies of environments affected by these aggregates be carried out.

One area of research that is sorely lacking is the fate of oil that is undispersed by OMAs when fine sediment is present. Fine sediment is known not only for increasing oil dispersion through OMA formation, but it is also known for stabilizing emulsifications of oil and water.

Therefore, it is hypothesized that the presence of mineral fines in sandy beach environments will facilitate the submergence of floating oil as macroscopic aggregates when compared to beach environments where only sand is present. We postulate that mineral fines will first stabilize floating oil emulsions, thereby increasing its ability to retain sand particles. The resultant density increase will cause the oil to submerge more rapidly, and at lower mixing energy levels than oil that is not exposed to mineral fines. Through testing this hypothesis, we can gain valuable insight which will aid in predicting of the submergence of oil as a result of future oil spills affecting nearshore environments, therefore providing key information to assist remediation decision makers. Understanding how mineral fines affect the submergence of oil is crucial because elevated concentrations of mineral fines can be introduced to nearshore environments either naturally, as a result of discharges from rivers with sediment-laden waters, or artificially, through the engineered enhancement of OMAs through sediment slurry application.

4.4   Concluding remarks

In a review on the various threats to sandy beaches, Defeo et al. (2009) asserted that "*oil spills are potentially the most destructive pollution source impacting sandy beaches, affecting all trophic levels.*" In order to mitigate the damage that oil spills may cause to sandy beaches, which support diverse ecosystems as well as critical fishing and tourism economies, it is important to have a robust conversation about the various ways that oil may affect these beaches. The intent of this work is to encourage open discussions and collaboration between researchers that seek to understand either microscopic or macroscopic aggregates independently. Due to the similarities between these two classes of aggregates, the authors

believe that either group could benefit substantially by furthering their understanding of the research that has been carried out by the other group. Our hope is that by fostering this relationship, more inclusive decision making process can be used to determine remediation activities for oiled sandy shorelines.

References

ASTM D3279-12. Standard Test Method for n-Heptane Insolubles. ASTM International.

Abkarian, M., Protière, S., Aristoff, J.M., Stone, H.A., 2013. Gravity-induced encapsulation of liquids by destabilization of granular rafts. Nature communications 4, 1895.

Aeppli, C., Carmichael, C.A., Nelson, R.K., Lemkau, K.L., Graham, W.M., Redmond, M.C., Valentine, D.L., Reddy, C.M., 2012. Oil weathering after the Deepwater Horizon disaster led to the formation of oxygenated residues. Environ Sci Technol 46, 8799-8807.

Ajijolaiya, L.O., Hill, P.S., Islam, M.R., 2007. Qualitative Understanding of the Mechanism of Oil Mineral Interaction as Potential Oil Spill Countermeasure—A Review. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 29, 499-509.

Ajijolaiya, L.O., Hill, P.S., Khelifa, A., Islam, R.M., Lee, K., 2006. Laboratory investigation of the effects of mineral size and concentration on the formation of oil-mineral aggregates. Mar Pollut Bull 52, 920-927.

Bandara, U.C., Yapa, P.D., Xie, H., 2011. Fate and transport of oil in sediment laden marine waters. J Hydro-Environ Res 5, 145-156.

Barron, M.G., 2012. Ecological impacts of the Deepwater Horizon oil spill: implications for immunotoxicity. Toxicologic pathology 40, 315-320.

Bernabeu, A., De la Fuente, M.N., Rey, D., Rubio, B., Vilas, F., Medina, R., González, M., 2006. Beach morphodynamics forcements in oiled shorelines: coupled physical and chemical processes during and after fuel burial. Mar Pollut Bull 52, 1156-1168.

Bernabeu, A.M., Fernández-Fernández, S., Bouchette, F., Rey, D., Arcos, A., Bayona, J.M., Albaiges, J., 2013. Recurrent arrival of oil to Galician coast: The final step of the Prestige deep oil spill. Journal of Hazardous Materials 250–251, 82-90.

Bernabeu, A.M., Rey, D., Rubio, B., Vilas, F., Domínguez, C., Bayona, J.M., Albaigés, J., 2009. Assessment of cleanup needs of oiled sandy beaches: lessons from the Prestige oil spill. Environ Sci Technol 43, 2470-2475.

Bhattacharya, D., Clement, T.P., Dhanasekaran, M., 2016. Evaluating the neurotoxic effects of Deepwater Horizon oil spill residues trapped along Alabama's beaches. Life Sci 155, 161-166.

Boglaienko, D., Tansel, B., 2015. Instantaneous stabilization of floating oils by surface application of natural granular materials (beach sand and limestone). Mar Pollut Bull 91, 107-112.

Boglaienko, D., Tansel, B., 2016a. Gravity induced densification of floating crude oil by granular materials: Effect of particle size and surface morphology. Sci Total Environ 556, 146-153.

Boglaienko, D., Tansel, B., 2016b. Partitioning of fresh crude oil between floating, dispersed and sediment phases: Effect of exposure order to dispersant and granular materials. Journal of environmental management 175, 40-45.

Bragg, J.R., Owens, E.H., 1995. Shoreline cleansing by interactions between oil and fine mineral particles, International Oil Spill Conference. American Petroleum Institute, pp. 219-227.

Bragg, J.R., Yang, S.H., 1995. Clay-oil flocculation and its role in natural cleansing in Prince William Sound following the Exxon Valdez oil spill, Exxon Valdez oil spill: Fate and effects in Alaskan waters. ASTM International.

Burns III, G.H., Benson, C.B., Eason, T., Michel, J., Kelly, S., Benggio, B., Ploen, M., 1995. Recovery of submerged oil at San Juan, Puerto Rico 1994, International Oil Spill Conference. American Petroleum Institute, pp. 551-557.

Cai, Z., Fu, J., Liu, W., Fu, K., O'Reilly, S., Zhao, D., 2016. Effects of oil dispersants on settling of marine sediment particles and particle-facilitated distribution and transport of oil components. Mar Pollut Bull.

Chapman, H., Purnell, K., Law, R.J., Kirby, M.F., 2007. The use of chemical dispersants to combat oil spills at sea: A review of practice and research needs in Europe. Mar Pollut Bull 54, 827-838.

Charrié-Duhaut, A., Lemoine, S., Adam, P., Connan, J., Albrecht, P., 2000. Abiotic oxidation of petroleum bitumens under natural conditions. Organic Geochemistry 31, 977-1003.

Chen, L., Zhou, Y., Wang, X., Zwicker, T., Lu, J., 2013. Enhanced oil–mineral aggregation with modified bentonite. Water Science and Technology 67, 1581-1589.

Cirer-Costa, J.C., 2015. Tourism and its hypersensitivity to oil spills. Mar Pollut Bull 91, 65-72.

Clement, T.P., John, G.F., Yin, F., 2017. Assessing the increase in background oil contamination levels in Alabama's nearshore beach environment resulting from the Deepwater Horizon oil spill, Oil Spill Science and Technology (Second Edition). Elsevier Publishers, pp. 851-888.

Cloutier, D., Hill, P.R., Amos, C.L., Lee, K., 2003. Annular flume experiments on oil-mineral aggregates: an oil spill countermeasure on low energy shorelines. Proceedings from the 2nd International Symposium on Contaminate Sediments, 129-133.

Daly, K.L., Passow, U., Chanton, J., Hollande, D., 2016. Assessing the impacts of oil-associated marine snow formation and sedimentation during and after the Deepwater Horizon oil spill. Anthropocene 13, 18-33.

Dalyander, P.S., Long, J.W., Plant, N.G., Thompson, D.M., 2014. Assessing mobility and redistribution patterns of sand and oil agglomerates in the surf zone. Mar Pollut Bull 80, 200-209.

Dalyander, P.S., Plant, N.G., Long, J.W., McLaughlin, M., 2015. Nearshore dynamics of artificial sand and oil agglomerates. Mar Pollut Bull 96, 344-355.

Danchuk, S., Willson, C.S., 2011. Influence of Seasonal Variability of Lower Mississippi River Discharge, Temperature, Suspended Sediments, and Salinity on Oil-Mineral Aggregate Formation. Water Environment Research 83, 579-587.

Defeo, O., McLachlan, A., Schoeman, D.S., Schlacher, T.A., Dugan, J., Jones, A., Lastra, M., Scapini, F., 2009. Threats to sandy beach ecosystems: a review. Estuarine, Coastal and Shelf Science 81, 1-12.

Delvigne, G.A.L., 1987. Droplet Size Distribution of Naturally Dispersed Oil, in: Kuiper, J., Van Den Brink, W.J. (Eds.), Fate and Effects of Oil in Marine Ecosystems: Proceedings of the Conference on Oil Pollution Organized under the auspices of the International Association on Water Pollution Research and Control (IAWPRC) by the Netherlands Organization for Applied Scientific Research TNO Amsterdam, The Netherlands, 23–27 February 1987. Springer Netherlands, Dordrecht, pp. 29-40.

Delvigne, G.A.L., Sweeney, C.E., 1988. Natural dispersion of oil. Oil and Chemical Pollution 4, 281-310.

Devadoss, R.S., Sannasiraj, S., Murali, K., 2009. Laboratory Investigation of Clay Mineral Fines as Dispersant for Combating Oil Spill, ASME 2009 28th International Conference on Ocean, Offshore and Arctic Engineering. American Society of Mechanical Engineers, pp. 313-317.

Dickey, R., Huettel, M., 2016. Seafood and Beach Safety in the Aftermath of the Deepwater Horizon Oil Spill. OCEANOGRAPHY 29, 196-203.

Dubansky, B., Whitehead, A., Miller, J.T., Rice, C.D., Galvez, F., 2013. Multitissue molecular, genomic, and developmental effects of the Deepwater Horizon oil spill on resident Gulf killifish (Fundulus grandis). Environ Sci Technol 47, 5074-5082.

Dupuis, A., Ucan-Marin, F., 2015. A literature review on the aquatic toxicology of petroleum oil: An overview of oil properties and effects to aquatic biota, Res Doc. Canadian Science Advisory Secretariat (CSAS).

Elango, V., Urbano, M., Lemelle, K.R., Pardue, J.H., 2014. Biodegradation of MC252 oil in oil:sand aggregates in a coastal headland beach environment. Front Microbiol 5.

Evans, M., Liu, J., Bacosa, H., Rosenheim, B.E., Liu, Z., 2016. Petroleum hydrocarbon persistence following the Deepwater Horizon oil spill as a function of shoreline energy. Mar Pollut Bull.

Florida Department of Environmental Protection (FDEP), National Oceanic and Atmospheric Administration (NOAA), US Department of Interior (DOI), 1997. Damage Assessment and Restoration Plan / Environmental Assessment for the August 10, 1993 Tampa Bay Oil Spill.

Fitzpatrick, F.A., Boufadel, M.C., Johnson, R., Lee, K.W., Graan, T.P., Bejarano, A.C., Zhu, Z., Waterman, D., Capone, D.M., Hayter, E., 2015. Oil-particle interactions and submergence from crude oil spills in marine and freshwater environments: review of the science and future research needs. US Geological Survey.

Fu, J., Gong, Y., Zhao, X., O'Reilly, S., Zhao, D., 2014. Effects of oil and dispersant on formation of marine oil snow and transport of oil hydrocarbons. Environ Sci Technol 48, 14392-14399.

Gong, Y., Zhao, X., Cai, Z.Q., O'Reilly, S.E., Hao, X., Zhao, D., 2014. A review of oil, dispersed oil and sediment interactions in the aquatic environment: Influence on the fate, transport and remediation of oil spills. Mar Pollut Bull 79, 16-33.

Goodman, R., 2003. Tar balls: the end state. Spill Sci Technol B 8, 117-121.

Gros, J., Reddy, C.M., Aeppli, C., Nelson, R.K., Carmichael, C.A., Arey, J.S., 2014. Resolving biodegradation patterns of persistent saturated hydrocarbons in weathered oil samples from the Deepwater Horizon disaster. Environ Sci Technol 48, 1628-1637.

Guidetti, P., Modena, M., La Mesa, G., Vacchi, M., 2000. Composition, abundance and stratification of macrobenthos in the marine area impacted by tar aggregates derived from the Haven oil spill (Ligurian Sea, Italy). Mar Pollut Bull 40, 1161-1166.

Gustitus, S.A., John, G.F., Clement, T.P., 2017. Effects of weathering on the dispersion of crude oil through oil-mineral aggregation. Sci Total Environ 587–588, 36-46.

Guyomarch, J., Le Floch, S., Merlin, F., 2002. Effect of suspended mineral load, water salinity and oil type on the size of oil-mineral aggregates in the presence of chemical dispersant. Spill Sci Technol B 8, 95-100.

Hansen, K.A., 2010. Research efforts for detection and recovery of submerged oil, Proceedings of the 33rdArctic and Marine Oil Spill Program, Technical Seminar. Ottawa, Ontario: Environment Canada, pp. 1055-1069.

Hansen, K.A., 2013. Submerged Oil Response. Coast Guard Journal of Safety & Security at Sea, Proceedings of the Marine Safety & Security Council 70.

Hansen, K.A., Guidroz, L., Hazel, B., Fitzpatrick, M., Johnson, G.W., 2014. Sunken Oil Recovery System Recommendations, International Oil Spill Conference Proceedings. American Petroleum Institute, pp. 2014-2023.

Harvey, R., Young, L., 1980. Enumeration of particle-bound and unattached respiring bacteria in the salt marsh environment. Applied and Environmental Microbiology 40, 156-160.

Hayworth, J.S., Clement, T.P., 2011. BP's Operation Deep Clean-Could Dilution be the Solution to Beach Pollution? Environ Sci Technol 45, 4201-4202.

Hayworth, J.S., Clement, T.P., John, G.F., Yin, F., 2015. Fate of Deepwater Horizon oil in Alabama's beach system: Understanding physical evolution processes based on observational data. Mar Pollut Bull 90, 95-105.

Hayworth, J.S., Clement, T.P., Valentine, J.F., 2011. Deepwater Horizon oil spill impacts on Alabama beaches. Hydrol Earth Syst Sc 15, 3639-3649.

Hendricks, C.W., 1974. Sorption of heterotrophic and enteric bacteria to glass surfaces in the continuous culture of river water. Applied microbiology 28, 572-578.

Hill, P.S., Khelifa, A., Lee, K., 2002. Time scale for oil droplet stabilization by mineral particles in turbulent suspensions. Spill Sci Technol B 8, 73-81.

Huba, A.K., Gardinali, P.R., 2016. Characterization of a crude oil weathering series by ultrahigh-resolution mass spectrometry using multiple ionization modes. Sci Total Environ 563–564, 600-610.

Jahns, H.O., Bragg, J.R., Dash, L.C., Owens, E.H., 1991. Natural cleaning of shorelines following the Exxon Valdez spill, International Oil Spill Conference. American Petroleum Institute, pp. 167-176.

Jernelöv, A., Lindén, O., 1981. Ixtoc I: a case study of the world's largest oil spill. Ambio, 299-306.

Jézéquel, R., Merlin, F.-X., Lee, K., 1999. The influence of microorganisms on oil-mineral fine interactions in low-energy coastal environment, International oil spill conference. American Petroleum Institute, pp. 771-775.

John, G.F., Han, Y., Clement, T.P., 2016. Weathering patterns of polycyclic aromatic hydrocarbons contained in submerged Deepwater Horizon oil spill residues when re-exposed to sunlight. Sci Total Environ 573, 189-202.

Junoy, J., Castellanos, C., Manuel Viéitez, J., Riera, R., 2013. Seven years of macroinfauna monitoring at Ladeira beach (Corrubedo Bay, NW Spain) after the Prestige oil spill*. Oceanologia 55, 393-407.

Kalke, R.D., Duke, T.A., Flint, R.W., 1982. Weathered IXTOC I oil effects on estuarine benthos. Estuarine, Coastal and Shelf Science 15, 75-84.

Kepkay, P.E., Bugden, J.B.C., Lee, K., Stoffyn-Egli, P., 2002. Application of ultraviolet fluorescence spectroscopy to monitor oil-mineral aggregate formation. Spill Sci Technol B 8, 101-108.

Khelifa, A., Fieldhouse, B., Wang, Z., Yang, C., Landriault, M., Fingas, M., Brown, C.E., Gamble, L., Pjontek, D., 2007. A laboratory study on formation of oil-SPM aggregates using the NIST standard reference material 1941b, Arctic and Marine Oil Spill Program Technical Seminar. Environment Canada; 1999, p. 35.

Khelifa, A., Fingas, M., Brown, C., 2008. Effects of dispersants on Oil-SPM aggregation and fate in US coastal Waters. Final Report Grant Number: NA04NOS4190063.

Khelifa, A., Hill, P.S., Lee, K., 2005a. A comprehensive numerical approach to predict oil-mineral aggregate (OMA) formation following oil spills in aquatic environments, International Oil Spill Conference. American Petroleum Institute, pp. 873-877.

Khelifa, A., Stoffyn-Egli, P., Hill, P.S., Lee, K., 2002. Characteristics of oil droplets stabilized by mineral particles: Effects of oil type and temperature. Spill Sci Technol B 8, 19-30.

Khelifa, A., Stoffyn-Egli, P., Hill, P.S., Lee, K., 2003. Characteristics of oil droplets stabilized by mineral particles: the effect of salinity, International Oil Spill Conference. American Petroleum Institute, pp. 963-970.

Khelifa, A., Stoffyn-Egli, P., Hill, P.S., Lee, K., 2005b. Effects of salinity and clay type on oil-mineral aggregation. Mar Environ Res 59, 235-254.

Kimes, N.E., Callaghan, A.V., Suflita, J.M., Morris, P.J., 2014. Microbial transformation of the Deepwater Horizon oil spill—past, present, and future perspectives. Front Microbiol 5, 603.

Kirchman, D., Mitchell, R., 1982. Contribution of particle-bound bacteria to total microheterotrophic activity in five ponds and two marshes. Applied and Environmental Microbiology 43, 200-209.

Kiruri, L.W., Dellinger, B., Lomnicki, S., 2013. Tar balls from Deep Water Horizon oil spill: environmentally persistent free radicals (EPFR) formation during crude weathering. Environ Sci Technol 47, 4220-4226.

Kostka, J.E., Prakash, O., Overholt, W.A., Green, S.J., Freyer, G., Canion, A., Delgardio, J., Norton, N., Hazen, T.C., Huettel, M., 2011. Hydrocarbon-degrading bacteria and the bacterial community response in Gulf of Mexico beach sands impacted by the Deepwater Horizon oil spill. Applied and Environmental Microbiology 77, 7962-7974.

Kujawinski, E.B., Kido Soule, M.C., Valentine, D.L., Boysen, A.K., Longnecker, K., Redmond, M.C., 2011. Fate of dispersants associated with the Deepwater Horizon oil spill. Environ Sci Technol 45, 1298-1306.

Le Floch, S., Guyomarch, J., Merlin, F.-X., Stoffyn-Egli, P., Dixon, J., Lee, K., 2002. The influence of salinity on oil–mineral aggregate formation. Spill Sci Technol B 8, 65-71.

Lee, K., Li, Z., Robinson, B., Kepkay, P.E., Blouin, M., Doyon, B., 2011. Field trials of in-situ oil spill countermeasures in ice-infested waters, International oil spill conference proceedings (IOSC). American Petroleum Institute, p. abs160.

Lee, K., Lunel, T., Wood, P., Swannell, R., Stoffyn-Egli, P., 1997. Shoreline cleanup by acceleration of clay-oil flocculation processes, International oil spill conference. American Petroleum Institute, pp. 235-240.

Lee, K., Stoffyn-Egli, P., Tremblay, G.H., Owens, E.H., Sergy, G.A., Guenette, C.C., Prince, R.C., 2003a. Oil-mineral aggregate formation on oiled beaches: Natural attenuation and sediment relocation. Spill Sci Technol B 8, 285-296.

Lee, K., Stoffyn-Egli, P., Wood, P., Lunel, T., 1998. Formation and structure of oil-mineral fines aggregates in coastal environments.

Lee, K., Weise, A.M., St-Pierre, S., 1996. Enhanced oil biodegradation with mineral fine interaction. Spill Sci Technol B 3, 263-267.

Lee, K., Wohlgeschaffen, G., Tremblay, G.H., Johnson, B.T., Sergy, G.A., Prince, R.C., Guénette, C.C., Owens, E.H., 2003b. Toxicity evaluation with the Microtox® test to assess the impact of in situ oiled shoreline treatment options: natural attenuation and sediment relocation. Spill Sci Technol B 8, 273-284.

Lee, K., Zheng, Y., Merlin, F.X., Li, Z., Niu, H., King, T., Robinson, B., Kepkay, P.E., Wohlgeschaffen, G.D., Doane, R., 2012. Combining Mineral Fines with Chemical Dispersants to Disperse Oil in Low Temperature and Low Mixing Environments, Including the Arctic. US Department of the Interior, Bureau of Safety and Environmental Enforcement (BSEE).

Lee, R.F., 2003. Photo-oxidation and photo-toxicity of crude and refined oils. Spill Sci Technol B 8, 157-162.

Lee, S., Mackay, D., Bonville, F., Joner, E., Shiu, W., 1989. A study of the long-term weathering of submerged and overwashed oil. Proceedings of the twelfth Arctic and Marine Oilspill Program (AMOP) Technical Seminar, 33-60.

Lemelle, K.R., Elango, V., Pardue, J.H., 2014. Distribution, characterization, and exposure of MC252 oil in the supratidal beach environment. Environmental toxicology and chemistry 33, 1544-1551.

Li, Z.K., Kepkay, P., Lee, K., King, T., Boufadel, M.C., Venosa, A.D., 2007. Effects of chemical dispersants and mineral fines on crude oil dispersion in a wave tank under breaking waves. Mar Pollut Bull 54, 983-993.

Linden, O., 1975. Acute effects of oil and oil/dispersant mixture on larvae of Baltic herring. Ambio, 130-133.

Liu, J., Zhang, L., Xu, Z., Masliyah, J., 2006. Colloidal interactions between asphaltene surfaces in aqueous solutions. Langmuir 22, 1485-1492.

Liu, Z., Liu, J., Zhu, Q., Wu, W., 2012. The weathering of oil after the Deepwater Horizon oil spill: insights from the chemical composition of the oil from the sea surface, salt marshes and sediments. Environmental Research Letters 7, 035302.

Loh, A., Shim, W.J., Ha, S.Y., Yim, U.H., 2014. Oil-suspended particulate matter aggregates: Formation mechanism and fate in the marine environment. Ocean Science Journal 49, 329-341.

Loh, A., Yim, U.H., 2016. A review of the effects of particle types on oil-suspended particulate matter aggregate formation. Ocean Science Journal 51, 535-548.

Ma, X., Cogswell, A., Li, Z., Lee, K., 2008. Particle Size Analysis of Dispersed Oil and Oil-Mineral Aggregates with an Automated Ultraviolet Epi-Fluorescence Microscopy System. Environmental technology 29, 739-748.

Michel, J., 2006. Assessment and recovery of submerged oil: Current state analysis. US Coast Guard Research & Development Center, Groton, CT.

Michel, J., Gait, J., 1995. Conditions under which floating slicks can sink in marine settings, International Oil Spill Conference. American Petroleum Institute, pp. 573-576.

Michel, J., Owens, E.H., Zengel, S., Graham, A., Nixon, Z., Allard, T., Holton, W., Reimer, P.D., Lamarche, A., White, M., 2013. Extent and degree of shoreline oiling: Deepwater Horizon oil spill, Gulf of Mexico, USA. PloS one 8, e65087.

Miranda, L.S., Moreira, Í.T.A., Oliveira, O.M.C., Santos, C.P., Pinheiro, S.M.M., Oliveira, L.M.L., Martins, A.B.O., Filho, M.S.C., 2016. Oil-suspended particulate material aggregates as a tool in preventing potential ecotoxicological impacts in the São Paulo river, Todos os Santos Bay, Bahia, Brazil: Influence of salinity and suspended particulate material. Mar Pollut Bull 112, 91-97.

Moller, T., 1992. Recent experience of oil sinking.

Moreira, Í.T.A., Oliveira, O.M.C., Silva, C.S., Rios, M.C., Queiroz, A.F.S., Assunção, R.V., Carvalho, A.P.N., 2015. Chemometrics applied in laboratory study on formation of oil–spm aggregates (OSAs) — A contribution to ecological evaluation. Microchemical Journal 118, 198-202.

Mulabagal, V., Yin, F., John, G.F., Hayworth, J.S., Clement, T.P., 2013. Chemical fingerprinting of petroleum biomarkers in Deepwater Horizon oil spill samples collected from Alabama shoreline. Mar Pollut Bull 70, 147-154.

Niu, H., Lee, K., Boufadel, M.C., Zhao, L., Robinson, B., 2014. In Situ Oil Spill Countermeasures in Ice-Infested Waters: A Modeling Study of the Fate/Behaviours of Spilled Oil, International Oil Spill Conference Proceedings. American Petroleum Institute, pp. 1215-1225.

Niu, H., Li, Z., Lee, K., Kepkay, P., Mullin, J., 2010. A method for assessing environmental risks of oil-mineral-aggregate to benthic organisms. Human and Ecological Risk Assessment 16, 762-782.

Niu, H., Li, Z., Lee, K., Kepkay, P., Mullin, J.V., 2011. Modelling the transport of oil–mineral-aggregates (OMAs) in the marine environment and assessment of their potential risks. Environmental modeling & assessment 16, 61-75.

Nixon, Z., Zengel, S., Baker, M., Steinhoff, M., Fricano, G., Rouhani, S., Michel, J., 2016. Shoreline oiling from the Deepwater Horizon oil spill. Mar Pollut Bull 107, 170-178.

Omotoso, O.E., Munoz, V.A., Mikula, R.J., 2002. Mechanisms of crude oil–mineral interactions. Spill Sci Technol B 8, 45-54.

Operational Science and Advisory Team (OSAT-1), 2010. Summary Report for Sub-Sea and Sub-Surface Oil and Dispersant Detection: Sampling and Monitoring Report to the Federal On-Scene Coordinator, Deepwater Horizon, December, 2010.

Operational Science and Advisory Team (OSAT-2), 2011. Summary Report for Fate and Effects of Remnant Oil in the Beach Environment, Report to the Federal On-Scene Coordinator, Deepwater Horizon.

Operational Science and Advisory Team (OSAT-3), 2013. Investigation of Recurring Residual Oil in Discrete Shoreline Areas in the Eastern Area of Responsibility.

Oudot, J., Merlin, F., Pinvidic, P., 1998. Weathering rates of oil components in a bioremediation experiment in estuarine sediments. Mar Environ Res 45, 113-125.

Owens, E.H., 1999. The interaction of fine particles with stranded oil. Pure and Applied Chemistry 71, 83-93.

Owens, E.H., Lee, K., 2003. Interaction of oil and mineral fines on shorelines: review and assessment. Mar Pollut Bull 47, 397-405.

Owens, E.H., Michel, J., Davis Jr, R.A., Stritzke, K., 1995. Beach cleaning and the role of technical support in the 1993 Tampa Bay spill, International Oil Spill Conference. American Petroleum Institute, pp. 627-634.

Owens, E.H., Taylor, E., Graham, A., Castle, R.W., 2011. Sand beach treatment studies and field trials conducted during the Deepwater Horizon-Macondo response operation, International Oil Spill Conference Proceedings (IOSC). American Petroleum Institute, p. abs265.

Owens, E.H., Taylor, E., Humphrey, B., 2008. The persistence and character of stranded oil on coarse-sediment beaches. Mar Pollut Bull 56, 14-26.

Passow, U., 2016. Formation of rapidly-sinking, oil-associated marine snow. Deep-Sea Res Pt Ii 129, 232-240.

Payne, J., Kirstein, B., Clayton, J., Clary, C., Redding, R., McNabb, D., Farmer, G., 1987. Integration of suspended particulate matter and oil transportation study. Final Report, Report to Minerals Management Service, MMS, 87-0083.

Payne, J.R., 1989. Oil-ice Sediment Interactions During Freeze-up and Break-up: Final Report. US Department of Commerce, National Oceanic and Atmospheric Administration, Ocean Assessments Division, Alaska Office.

Payne, J.R., Clayton, J.R., Kirstein, B.E., 2003. Oil/suspended particulate material interactions and sedimentation. Spill Sci Technol B 8, 201-221.

Pendergraft, M.A., Rosenheim, B.E., 2014. Varying relative degradation rates of oil in different forms and environments revealed by ramped pyrolysis. Environ Sci Technol 48, 10966-10974.

Pequegnat, W.E., Jeffrey, L.M., 1979. Petroleum in deep benthic ecosystems of the Gulf of Mexico and Caribbean Sea. Contributions in Marine Science 22.

Plant, N.G., Long, J.W., Dalyander, P.S., Thompson, D.M., Raabe, E.A., 2013. Application of a hydrodynamic and sediment transport model for guidance of response efforts related to the Deepwater Horizon oil spill in the Northern Gulf of Mexico along the coast of Alabama and Florida. US Geological Survey.

Poirier, O.A., Thiel, G.A., 1941. Deposition of free oil by sediments settling in sea water. AAPG Bulletin 25, 2170-2180.

Popper, K.R., 1963. Conjectures and Refutations. Routledge & Kegan Paul, London.

Poteau, S., Argillier, J.-F., Langevin, D., Pincet, F., Perez, E., 2005. Influence of pH on stability and dynamic properties of asphaltenes and other amphiphilic molecules at the oil-water interface. Energy & Fuels 19, 1337-1341.

Prince, R., Lessard, R., Clark, J., 2003. Bioremediation of marine oil spills. Oil & Gas Science and Technology 58, 463-468.

Prince, R., Varadaraj, R., Fiocco, R., Lessard, R., 1999. Bioremediation as an oil spill response tool. Environmental technology 20, 891-896.

Quigg, A., Passow, U., Chin, W.C., Xu, C., Doyle, S., Bretherton, L., Kamalanathan, M., Williams, A.K., Sylvan, J.B., Finkel, Z.V., 2016. The role of microbial exopolymers in determining the fate of oil and chemical dispersants in the ocean. Limnology and Oceanography Letters 1, 3-26.

Raimondo, S., Hemmer, B.L., Lilavois, C.R., Krzykwa, J., Almario, A., Awkerman, J.A., Barron, M.G., 2015. Effects of Louisiana crude oil on the sheepshead minnow (Cyprinodon variegatus) during a life-cycle exposure to laboratory oiled sediment. Environmental toxicology.

Ramachandran, S.D., Hodson, P.V., Khan, C.W., Lee, K., 2004. Oil dispersant increases PAH uptake by fish exposed to crude oil. Ecotoxicology and Environmental Safety 59, 300-308.

Ramseur, J.L., 2010. Deepwater Horizon oil spill: the fate of the oil. Congressional Research Service, Library of Congress Washington, DC.

Rasband, W.S., 2016. ImageJ. U.S. National Institutes of Health, Bethesda, Maryland, USA.

Rios, M.C., Moreira, Í.T.A., Oliveira, O.M.C., Pereira, T.S., de Almeida, M., Trindade, M.C.L.F., Menezes, L., Caldas, A.S., 2017. Capability of Paraguaçu estuary (Todos os Santos Bay, Brazil) to form oil–SPM aggregates (OSA) and their ecotoxicological effects on pelagic and benthic organisms. Mar Pollut Bull 114, 364-371.

Rodriguez-r, L.M., Overholt, W.A., Hagan, C., Huettel, M., Kostka, J.E., Konstantinidis, K.T., 2015. Microbial community successional patterns in beach sands impacted by the Deepwater Horizon oil spill. The ISME journal.

Ruddy, B.M., Huettel, M., Kostka, J.E., Lobodin, V.V., Bythell, B.J., McKenna, A.M., Aeppli, C., Reddy, C.M., Nelson, R.K., Marshall, A.G., Rodgers, R.P., 2014. Targeted

Petroleomics: Analytical Investigation of Macondo Well Oil Oxidation Products from Pensacola Beach. Energy & Fuels 28, 4043-4050.

Savage, M., Ward, C., 1984. Chemical characteristics of laboratory produced tarballs. Mar Pollut Bull 15, 174-178.

Sergy, G.A., Guénette, C.C., Owens, E.H., Prince, R.C., Lee, K., 2003. In-situ treatment of oiled sediment shorelines. Spill Sci Technol B 8, 237-244.

Serrano, A., Sánchez, F., Preciado, I., Parra, S., Frutos, I., 2006. Spatial and temporal changes in benthic communities of the Galician continental shelf after the Prestige oil spill. Mar Pollut Bull 53, 315-331.

Silva, C.S., de Oliveira, O.M., Moreira, I.T., Queiroz, A.F., de Almeida, M., Silva, J.V., da Silva Andrade, I.O., 2015. Potential application of oil-suspended particulate matter aggregates (OSA) on the remediation of reflective beaches impacted by petroleum: a mesocosm simulation. Environmental Science and Pollution Research, 1-13.

Simister, R.L., Poutasse, C., Thurston, A., Reeve, J., Baker, M., White, H., 2015. Degradation of oil by fungi isolated from Gulf of Mexico beaches. Mar Pollut Bull 100, 327-333.

Sørensen, L., Melbye, A.G., Booth, A.M., 2014. Oil droplet interaction with suspended sediment in the seawater column: Influence of physical parameters and chemical dispersants. Mar Pollut Bull 78, 146-152.

Sterling, M.C., Bonner, J.S., Page, C.A., Fuller, C.B., Ernest, A.N.S., Autenrieth, R.L., 2004. Modeling crude oil droplet-sediment aggregation in nearshore waters. Environ Sci Technol 38, 4627-4634.

Stoffyn-Egli, P., Lee, K., 2002. Formation and characterization of oil-mineral aggregates. Spill Sci Technol B 8, 31-44.

Stout, S.A., Payne, J.R., Emsbo-Mattingly, S.D., Baker, G., 2016. Weathering of field-collected floating and stranded Macondo oils during and shortly after the Deepwater Horizon oil spill. Mar Pollut Bull 105, 7-22.

Sun, J., Khelifa, A., Zhao, C.C., Zhao, D.F., Wang, Z.D., 2014. Laboratory investigation of oil-suspended particulate matter aggregation under different mixing conditions. Sci Total Environ 473, 742-749.

Sun, J., Zheng, X.L., 2009. A review of oil-suspended particulate matter aggregation-a natural process of cleansing spilled oil in the aquatic environment. J Environ Monitor 11, 1801-1809.

Sun, J.A., Khelifa, A., Zheng, X.L., Wang, Z.D., So, L.L., Wong, S., Yang, C., Fieldhouse, B., 2010. A laboratory study on the kinetics of the formation of oil-suspended particulate matter aggregates using the NIST-1941b sediment. Mar Pollut Bull 60, 1701-1707.

Suneel, V., Ciappa, A., Vethamony, P., 2016. Backtrack modeling to locate the origin of tar balls depositing along the west coast of India. Sci Total Environ 569, 31-39.

Suneel, V., Vethamony, P., Naik, B., Krishna, M., Jadhav, L., 2015. Identifying the source of tar balls deposited along the beaches of Goa in 2013 and comparing with historical data collected along the west coast of India. Sci Total Environ 527, 313-321.

Suneel, V., Vethamony, P., Naik, B., Vinod Kumar, K., Sreenu, L., Samiksha, S., Tai, Y., Sudheesh, K., 2014. Source investigation of the tar balls deposited along the Gujarat coast, India, using chemical fingerprinting and transport modeling techniques. Environ Sci Technol 48, 11343-11351.

Tao, Z., Bullard, S., Arias, C., 2011. High numbers of Vibrio vulnificus in tar balls collected from oiled areas of the north-central Gulf of Mexico following the 2010 BP Deepwater Horizon oil spill. Ecohealth 8, 507-511.

Trudel, K., Belore, R.C., Mullin, J.V., Guarino, A., 2010. Oil viscosity limitation on dispersibility of crude oil under simulated at-sea conditions in a large wave tank. Mar Pollut Bull 60, 1606-1614.

Urbano, M., Elango, V., Pardue, J.H., 2013. Biogeochemical characterization of MC252 oil:sand aggregates on a coastal headland beach. Mar Pollut Bull 77, 183-191.

Van Loosdrecht, M., Lyklema, J., Norde, W., Zehnder, A., 1990. Influence of interfaces on microbial activity. Microbiological reviews 54, 75-87.

Venosa, A.D., Holder, E.L., 2013. Determining the dispersibility of South Louisiana crude oil by eight oil dispersant products listed on the NCP Product Schedule. Mar Pollut Bull 66, 73-77.

Venosa, A.D., King, D.W., Sorial, G.A., 2002. The baffled flask test for dispersant effectiveness: A round robin evaluation of reproducibility and repeatability. Spill Sci Technol B 7, 299-308.

Wang, P., Roberts, T.M., 2013. Distribution of surficial and buried oil contaminants across sandy beaches along NW Florida and Alabama coasts following the Deepwater Horizon oil spill in 2010. Journal of Coastal Research 29, 144-155.

Wang, W., Zheng, Y., Lee, K., 2013. Chemical dispersion of oil with mineral fines in a low temperature environment. Mar Pollut Bull 72, 205-212.

Wang, W.Z., Zheng, Y., Li, Z.K., Lee, K., 2011. PIV investigation of oil-mineral interaction for an oil spill application. Chem Eng J 170, 241-249.

Warnock, A.M., Hagen, S.C., Passeri, D.L., 2015. Marine tar residues: a review. Water, Air, & Soil Pollution 226, 1-24.

Weise, A., Nalewajko, C., Lee, K., 1999. Oil-mineral fine interactions facilitate oil biodegradation in seawater. Environmental technology 20, 811-824.

White, H.K., Wang, C.H., Williams, P.L., Findley, D.M., Thurston, A.M., Simister, R.L., Aeppli, C., Nelson, R.K., Reddy, C.M., 2016. Long-term weathering and continued oxidation of oil residues from the Deepwater Horizon spill. Mar Pollut Bull 113, 380-386.

Wise Jr, J.P., Wise, J.T., Wise, C.F., Wise, S.S., Gianios Jr, C., Xie, H., Thompson, W.D., Perkins, C., Falank, C., Wise Sr, J.P., 2014. Concentrations of the genotoxic metals, chromium and nickel, in whales, tar balls, oil slicks, and released oil from the gulf of Mexico in the immediate aftermath of the deepwater horizon oil crisis: is genotoxic metal exposure part of the deepwater horizon legacy? Environ Sci Technol 48, 2997-3006.

Wolfe, D.A., Hameedi, M., Galt, J., Watabayashi, G., Short, J., O'CLAIRE, C., Rice, S., Michel, J., Payne, J., Braddock, J., 1994. The fate of the oil spilled from the Exxon Valdez. Environ Sci Technol 28, 560A-568A.

Yin, F., John, G.F., Hayworth, J.S., Clement, T.P., 2015. Long-term monitoring data to describe the fate of polycyclic aromatic hydrocarbons in Deepwater Horizon oil submerged off Alabama's beaches. Sci Total Environ 508, 46-56.

Zhang, H.P., Khatibi, M., Zheng, Y., Lee, K., Li, Z.K., Mullin, J.V., 2010. Investigation of OMA formation and the effect of minerals. Mar Pollut Bull 60, 1433-1441.

Zhao, L., Boufadel, M.C., Geng, X., Lee, K., King, T., Robinson, B., Fitzpatrick, F., 2016. A-DROP: A predictive model for the formation of oil particle aggregates (OPAs). Mar Pollut Bull 106, 245-259.

Zuijdgeest, A., Huettel, M., 2012. Dispersants as used in response to the MC252-spill lead to higher mobility of polycyclic aromatic hydrocarbons in oil-contaminated Gulf of Mexico sand. PloS one 7, e50549.