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Key Points:

- Spilled oil can interact with suspended sediment to form either microscopic or macroscopic oil-sediment residues in nearshore environments
- Processes that control the formation, fate, and impacts of oil-sediment residues are reviewed and compared
- A uniform nomenclature is proposed to identify oil-sediment residues, and knowledge gaps and future research needs are discussed

Correspondence to:

T. P. Clement,
pclement@ua.edu

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Formation, Fate, and Impacts of Microscopic and Macroscopic Oil-Sediment Residues in Nearshore Marine Environments: A Critical Review

Sarah A. Gustitus¹ and T. Prabhakar Clement^{1,2} 

¹Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL, USA, ²Now at Department of Civil, Construction and Environmental Engineering, University of Alabama, Tuscaloosa, AL, USA

Abstract Crude oil that is spilled in marine environments often interacts with suspended sediments to form residues that can impact the recovery of the affected nearshore ecosystems. When spilled oil and sediment interact, they can form either small microscopic aggregates, commonly referred to as oil-particle aggregates, or large macroscopic agglomerates, referred to as sediment-oil agglomerates or sediment-oil mats. Although these different sized oil-sediment residues have similar compositions, they are formed under different conditions and have different fates in nearshore environments; the goal of this review is to synthesize our current understanding of these two types of residues. We believe that researchers who focus solely on studying either microscopic aggregates or macroscopic agglomerates could benefit from understanding the research findings available in the other field. In this study, we compare and contrast various processes that control the formation, fate, and impacts of these two types of residues in nearshore environments and point out some of the knowledge gaps in this field. Additionally, these residues have been referred to by many names in the past, leading to confusion and misconceptions at times. In this effort, we recommend a uniform nomenclature to distinguish them based on their physical size. Our overall aim is to bridge the gap between microscopic and macroscopic oil-sediment residue literature to foster a robust exchange of ideas, which we believe can lead to the development of efficient strategies for managing oil spills that affect nearshore environments.

1. Background

Oil spills that affect sandy marine 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. The development and execution of a plan for managing a coastal oil spill is a complex process that depends on several variables; one key variable is the type of residue that is formed when the oil reaches the shoreline. If the residues are in the form of small aggregates that can be easily degraded or diluted to nontoxic concentrations by natural processes, then the decision makers may let natural remediation processes take their course. On the contrary, if the oil accumulates to form large agglomerates that can persist for an extended period of time, then extensive human intervention will be required. In most cases, management of oil spills involves simultaneous human intervention and natural remediation at various scales, and balancing these processes to develop an ideal management strategy can be a complex challenge.

Of particular interest to the oil spill remediation community are microscopic and macroscopic residues that are formed from the interaction of oil with various types of sediments. Most oil-sediment residues are formed in nearshore environments where breaking waves and other turbulent shoreline forces facilitate the interaction of suspended sediments, such as sand, clay, or other fine minerals and organic particulates, with the floating oil. Microscopic aggregates, which we refer to in this study as oil-particle aggregates (OPAs), are typically <1 mm in size and are formed from interactions of oil with very fine sediments (Fitzpatrick et al., 2015; Gong et al., 2014; Sun & Zheng, 2009). The formation of microscopic aggregates is typically viewed as a beneficial process that can help facilitate natural remediation. Macroscopic oil-sediment agglomerates, which we refer to in this study as sediment-oil agglomerates (SOAs), are larger residues formed from the interaction of oil primarily with coarse sediments, although they may also be formed with large volumes of finer sediments, or a combination of coarse and fine sediments (Michel et al., 2013). SOAs are typically on the scale of several centimeters. Large patches of floating oil can also interact with sediments to produce massive sediment-oil mats (SOMs) that can reach up to several meters in length (Hayworth et al., 2015; Michel & Galt, 1995;

OSAT-2, 2011). Once formed, SOMs can be broken apart by various shoreline forces into centimeter-scale fragments to form SOAs. The formation of macroscopic agglomerates such as SOAs and SOMs is typically viewed as a harmful process that can hinder natural remediation.

2. Scope and Objectives

Although microscopic aggregates and macroscopic agglomerates are similar in composition, there are vast differences in the way they affect the recovery of oiled shorelines. The incorporation of oil into microscopic OPAs is a beneficial process because OPAs are easily dispersed, easy to degrade, and are expected to have minimal effects on marine organisms (Fitzpatrick et al., 2015). On the contrary, the formation of macroscopic SOMs/SOAs is a detrimental process because these aggregates hinder the degradation of oil, are toxic to marine organisms, and can lead to the periodic reoiling of the shoreline for years following a spill (Clement et al., 2017).

Almost all of the previous reviews that summarize the interactions between oil and sediment have focused exclusively on OPAs (Fitzpatrick et al., 2015; Gong et al., 2014; Loh et al., 2014; Loh & Yim, 2016; Sun & Zheng, 2009). More recently, Warnock et al. (2015) provided a general review of various forms of oil spill debris deposited on coastal environments; however, their study primarily focused on reviewing different forms of macroscopic marine tar residues formed from the Deepwater Horizon oil spill. Almost all previously published laboratory and/or field studies in this area focus exclusively on either microscopic aggregates or macroscopic agglomerates. Since OPAs (microscopic aggregates), SOAs, and SOMs (macroscopic agglomerates) are essentially oil-sediment mixtures formed at different scales, we believe that researchers who focus solely on either microscopic aggregates or macroscopic agglomerates could greatly benefit by understanding the research that has been carried out by the other group. Furthermore, we believe that a comprehensive analysis of these two classes of oil spill residues can lead to a better overall understanding of the transport of oil in coastal environments. Therefore, one of the objectives of this review is to bridge the divide between these two areas and promote a more robust conversation regarding the fate of oil in nearshore environments. In this study, we review the current state of knowledge regarding OPAs, SOAs, and SOMs with an aim to compare and contrast their implications for oil spill management and to identify current knowledge gaps, particularly those that could be remedied through collaboration between researchers who primarily focus on microscopic or macroscopic oil-sediment residues. Throughout this article, we will systematically review and analyze the differences between microscopic and macroscopic oil-sediment residues with respect to their formation, fate, and impacts in nearshore environments.

Examples of typical micrometer-scale OPAs, centimeter-scale SOAs, and meter-scale SOMs are shown in Figure 1. Also, Figure 2 shows a conceptual model of various types of oil residues that may be present in nearshore environments, including microscopic aggregates and macroscopic agglomerates, as well as other common forms of residues. Other forms of oil spill residues that can be found in nearshore environments 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 (Hayworth et al., 2011), oil-stained sediment that does not form distinct agglomerates, and highly weathered pelagic tar balls (Warnock et al., 2015). SOAs 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. Tar balls may be found floating in nearshore waters, as well as either deposited atop or buried along sandy beaches. This study focuses solely on residues that are mixtures of oil and sediment, and therefore, oil slicks, pelagic tar balls, floating mousse, floating tar material, and other forms of oil residues that are not aggregates are beyond the scope of this discussion.

Aggregations of oil with material of biological origin (e.g., 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 MOS is controlled by the presence of biologically mediated material such as the exopolymeric substances, mucous-rich particles, and/or other dead cells (Passow, 2016; Quigg et al., 2016), rather than by the presence of inorganic particulate matter (i.e., sediment). Additionally, 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. 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).

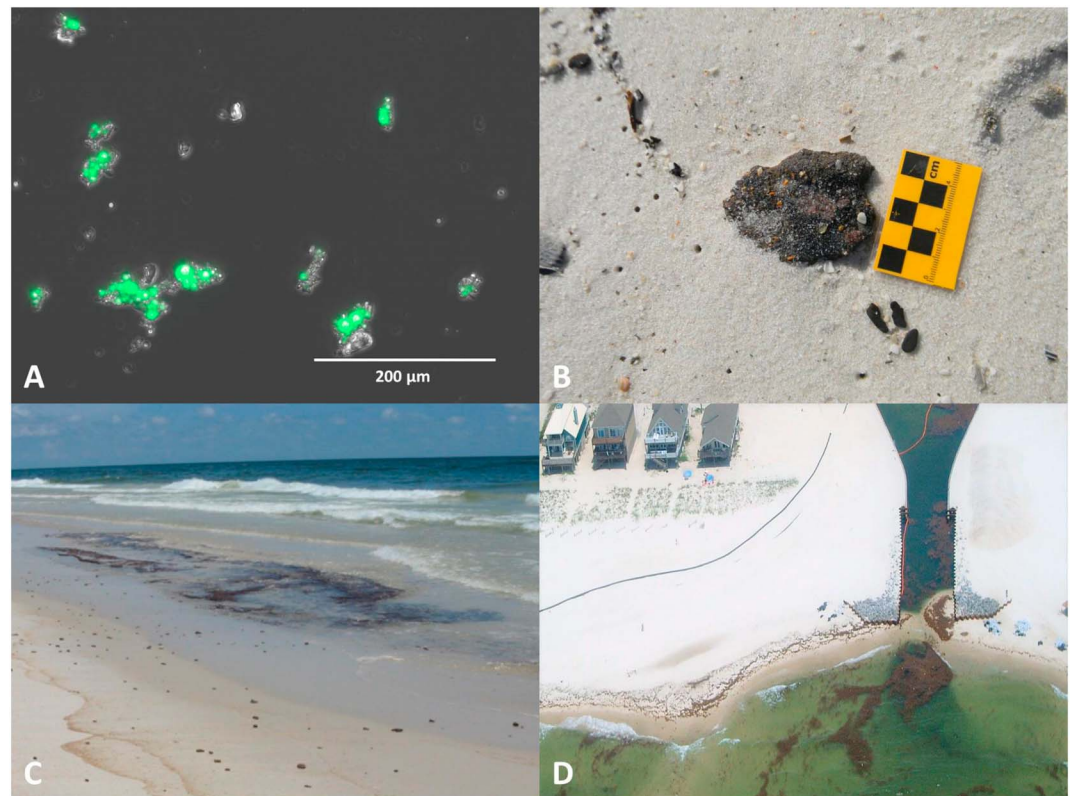


Figure 1. (a) Microscopic oil-particle aggregates (OPAs) viewed under fluorescent microscopy; (b) macroscopic sediment-oil agglomerate (SOA) on the beach; (c) a sediment-oil mat (SOM) near a shoreline, modified from OSAT-3 (2013); and (d) emulsified oil washing ashore.

3. Terminology

3.1. 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

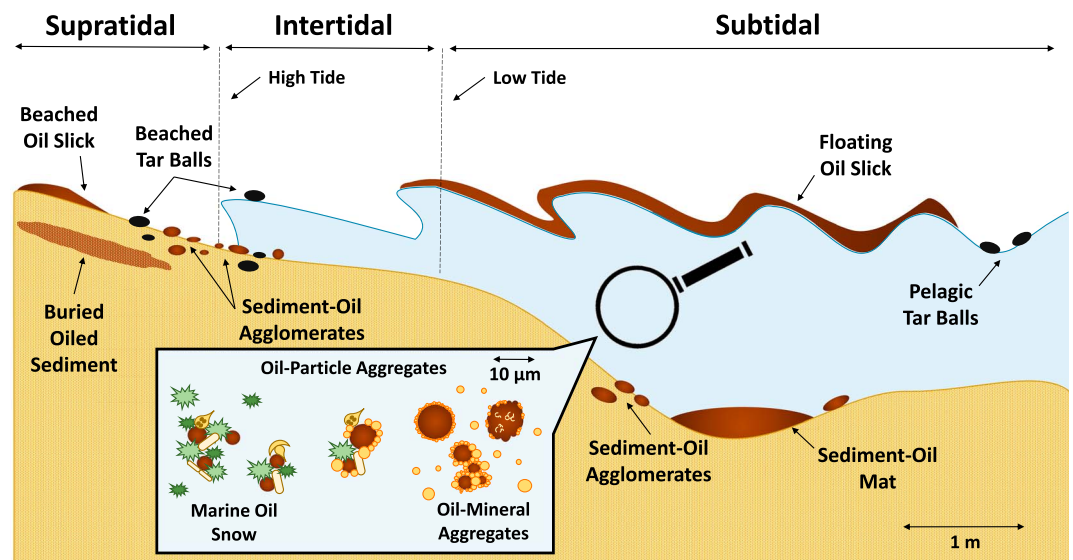


Figure 2. Conceptual model of the size and location of various oil residues found in nearshore environments.

“oil-sediment-seawater mixture.” Some subsequent studies examined interactions between oil and clay or other suspended particulate matter (Bassin & Ichiye, 1977; Payne et al., 1987). However, this phenomenon did not garner significant attention until the Exxon-Valdez oil spill when researchers observed the natural cleansing of oiled shorelines. In order to understand the mechanisms behind this natural remediation, investigations were carried out on how the formation of microscopic aggregates could have contributed to the cleansing process (Payne, 1989). In a preliminary study that investigated the role of these aggregates in remediating shorelines oiled by the Exxon-Valdez spill, the term “clay-oil flocs” was coined by Bragg and Yang (1995). Since this study, research effort 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 the observations made in both field and laboratory experiments when “fine-grained sediment and oil combine to form microaggregates.” 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), while other studies have used the term “oil-suspended particulate matter aggregates (OSA)” (Gong et al., 2014; Loh et al., 2014; Sun & Zheng, 2009). Recently, the term “oil-particle aggregate (OPA)” has become a preferred term to refer to microscopic aggregates (Fitzpatrick et al., 2015; Zhao et al., 2016). 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 formed microscopic aggregates exclusively with minerals (Khelifa et al., 2007; Khelifa et al., 2008; Sun et al., 2010; Sun et al., 2014). In real-world situations, it is difficult to exclude the possibility that organic material is incorporated into microscopic aggregates, and this has motivated the use of the more general term, OPA, to refer these aggregates.

3.2. Review of Nomenclature Used for Describing Macroscopic Agglomerates

Since macroscopic SOAs and SOMs are agglomerates of oil and minerals (sand and/or fine clays), they have also been occasionally referred to as “oil-mineral (sand) aggregates” in the literature (Stout et al., 2016). However, it is important to recognize that in almost all published studies, the term OMA has been primarily used for describing microscopic aggregates and is not intended to encompass any macroscopic agglomerates. Therefore, a different nomenclature is necessary to identify these two distinct size classes of oil-sediment residues. Until the Deepwater Horizon oil spill in 2010, SOAs were mostly lumped under the broad category of tar balls since there was no uniform term to specifically describe them (Michel & Galt, 1995). Similarly, SOMs were previously referred to simply as tar mats or submerged sedimented oil (OSAT-1, 2010). During the Deepwater Horizon spill, the terms “surface residual ball (SRB)” and “submerged oil mat (SOM)” were coined to describe these agglomerates. Initially, the OSAT-2 study introduced the term “small surface residual ball,” which was used to describe small oil-sand residues that escaped mechanical beach cleaning methods (OSAT-2, 2011). In later studies the term was condensed to SRB and used to describe oil residues on the scale of 1 mm–10 cm that continued to wash ashore throughout and after cleaning efforts (Dalyander et al., 2014; Hayworth et al., 2015; Plant et al., 2013; Yin et al., 2015). Another form of relatively dry SRB is also found on dry sandy beaches; these “onshore-SRBs” are formed when emulsified oil that is washed onshore is later buried under dry sand (Hayworth et al., 2011; Hayworth & Clement, 2011). In some published studies, oil-sediment aggregates that range from 10 cm to 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). Another type of aggregate that is similar to an SOM has been observed in beaches with very coarse sediments such as pebbles or gravel mixed with some sand. These aggregates are referred to as “asphalt pavements,” since they form a hard crust of weathered oil on their exterior, which shelters partially weathered oil on their interior (Owens et al., 2008). More recently, Dalyander et al. (2015) introduced another term, “sand and oil agglomerates (SOA),” to describe both SRBs and SOMs, and Bhattacharya et al. (2016) used the term “submerged residual oil mat” instead of SOM. It should be noted that currently the terms SRB, SRP, and SOM are almost exclusively used to describe Deepwater Horizon residues.

3.3. Lessons Learned and a Proposal for a Unified Nomenclature for Describing Oil-Sediment Residues

As discussed in the previous section, both microscopic and macroscopic oil-sediment residues have been referred to by several different names, and this can lead to confusion and misconceptions if they are not

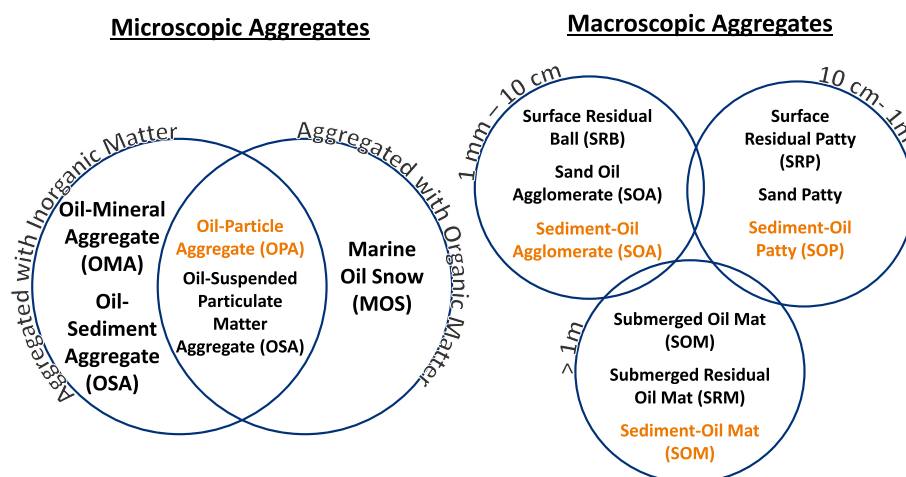


Figure 3. Summary of terminologies used for describing different types of oil-sediment aggregates and agglomerates. Terms highlighted in orange are recommended in this review to refer to the microscopic aggregates and macroscopic agglomerates discussed in this study.

properly understood. For example, a study completed by Omotoso et al. (2002) on OPA formation was later cited by Goodman (2003) as an example of tar ball formation, which is clearly confusing and perhaps misleading. Figure 3 summarizes the various nomenclature used to describe different types of microscopic and macroscopic oil-sediment residues. In this study, we make an attempt to learn from various discussions and provide recommendations to develop a unified nomenclature, which we believe can help promote better communication between different groups of investigators. Foremost, for clarity, we refer to microscopic residues as “aggregates,” and macroscopic residues as “agglomerates.” This distinction is adapted from the realms of materials research, where “agglomerates” are typically understood to be larger, less organized particulate structures than more organized, tightly bound microscopic “aggregates” (Walter, 2013).

Due to the prevalent use of “OPA” to refer to microscopic aggregates, especially in recent literature (Zhao et al., 2017), we recommend the continued use of this term to describe the aggregates that are on a scale of 1 mm or less and are formed primarily with oil and inorganic minerals or sediments. This term has been used to refer to natural microscopic aggregates that may include both organic and inorganic particulates, although it should be noted that oil and minerals are the major components in these aggregates.

Currently, the term “SRB” is used extensively to describe benthic agglomerate residues formed as a result of the Deepwater Horizon oil spill. However, limitations of this terminology are that the term “surface” is vague and “balls” implies spherical objects, while these agglomerates are commonly ellipsoidal or even irregularly shaped. Therefore, we propose a term, “sediment-oil agglomerates (SOAs)” to refer to these residues. This is a slight modification on the term “sand and oil agglomerates (SOAs)” used recently by Dalyander et al. (2015). This term has the advantage of using an acronym that is consistent with recently published literature, while accounting for the fact that these residues may be formed with sediments that can be mixture of sand, clay, and/or other particulate matter. In order to clearly distinguish SOAs from traditional tar balls, we define their properties as highly fragile (not rubbery); containing sticky, partially weathered oil; very high sediment content (~70% or more); and density values of $\sim 1.5 \text{ g/cm}^3$ or more. These parameters are based on the field characteristics of SOAs observed by various researchers (Mulabagal et al., 2013; Plant et al., 2013; Yin et al., 2015).

The less commonly used term, “surface residual patty (SRP),” is currently used to describe aggregates that are similar to SOAs but are on the scale of $\sim 10 \text{ cm} - 1 \text{ m}$. Once again, since the word “surface” is unclear, we propose the term “sediment-oil patties (SOPs)” to refer to these residues. SOPs are similar in composition to SOAs, although they tend to have relatively fresh oil at their core. The term “submerged oil mat (SOM)” is currently used to describe large, relatively immobile, sunken oil-sediment agglomerates on the scale of several meters. For the sake of uniformity, we propose the term “sediment-oil mats (SOMs),” which maintains the current commonly used acronym while also staying consistent with our proposed nomenclature. We recommend that the term “tar mat,” which is often used in popular literature, be avoided in scientific literature since it is less specific.

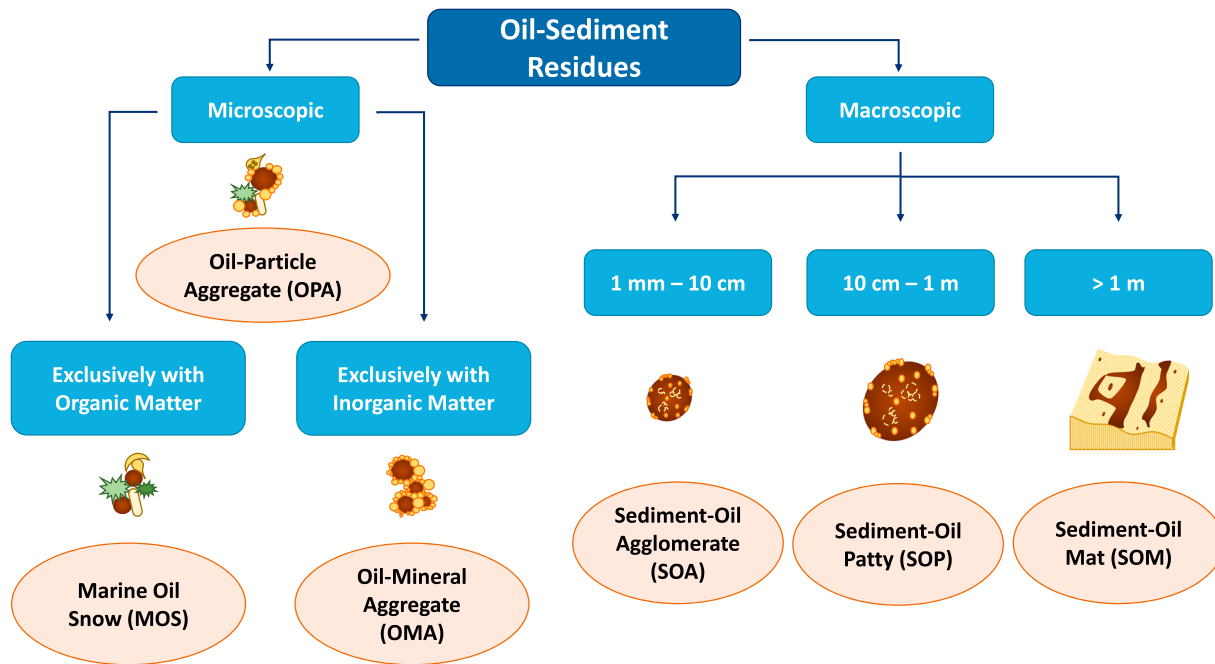


Figure 4. Proposed nomenclature for describing microscopic aggregates and macroscopic agglomerates.

Figure 4 summarizes the proposed nomenclature. In this study 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.

4. Formation

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

4.1. Formation of Microscopic Aggregates

OPAs characteristically form when oil interacts with very fine (typically $<10 \mu\text{m}$) sediment particles (Sun & 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 OPAs may play a role in the natural remediation of oiled shorelines, which was verified by subsequent laboratory studies (Bragg & Owens, 1995; Bragg & 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 OPA formation could also have played a role in natural remediation (Owens & Lee, 2003). The natural formation of OPAs in situ was first confirmed by microscopic observations that were made following the Sea Empress spill in 1996 (Lee et al., 1997). OPAs 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., 2003; Sergy et al., 2003). In addition to marine environments, OPAs have also been observed to form in freshwater systems impacted by oil spills (Fitzpatrick et al., 2015).

In order for OPAs to form, spilled oil must be dispersed into the water column as small droplets, following which the droplets must interact with and adhere to fine suspended minerals (see Figure 5). It has been recently identified that OPAs are formed when fine minerals penetrate into oil droplets at various depths to yield cohesive aggregates (Zhao et al., 2017). Nearshore environments are conducive to OPA formation

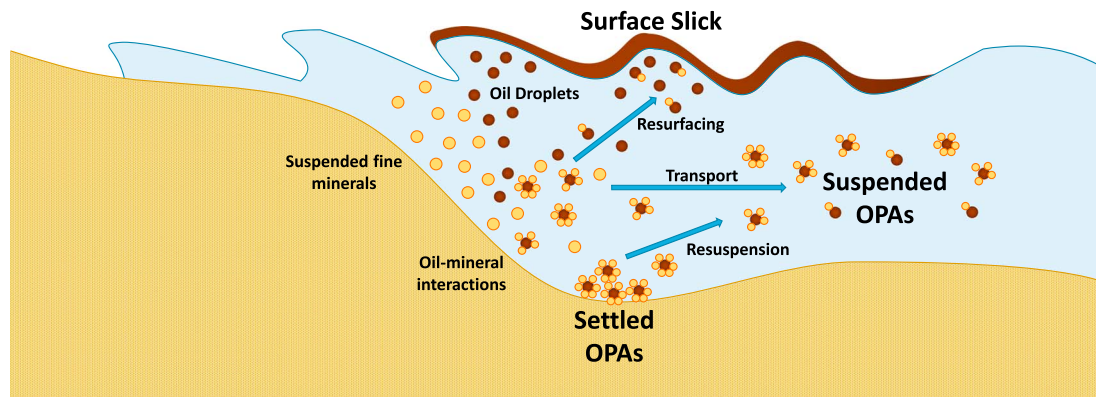


Figure 5. Conceptual model of how oil-particle aggregates (OPAs) form in the nearshore environment.

because the energy dissipated from breaking waves can break oil slicks into droplets while simultaneously keeping fine sediment in suspension (Delvigne & Sweeney, 1988; Sun et al., 2014). Depending on the environmental conditions, as well as the properties of both the oil and sediment, OPAs may appear in various sizes and shapes. Stoffyn-Egli and Lee (2002) identified and classified three main types of OPAs: droplet, solid, and flake. Droplet OPAs can form with either single or multiple droplets of oil. Single-droplet OPAs consist of a single spherical droplet of oil stabilized by sediment particles, whereas multiple-droplet OPAs contain several spherical oil droplets stabilized by sediment particles. Solid OPAs are aggregations of oil and mineral particles with irregular contours, where no clear individual droplets can be observed. Flake OPAs resemble membranes and are the least commonly observed type of OPA, having only been observed in laboratory experiments, and never in nature (Stoffyn-Egli & Lee, 2002). The size of an OPA is determined in part by its type. Droplet OPAs are typically a few micrometers wide and grow larger as more droplets are incorporated; solid OPAs are on the scale of tens of micrometers and can occasionally be found on the scale of hundreds of micrometers; flake OPAs are typically hundreds of micrometers and can stretch up to 1 mm in length (Stoffyn-Egli & Lee, 2002). The size of an OPA affects its buoyancy, which further determines how it is transported through the water column (i.e., rate of sedimentation or resurfacing). The size, type, and, most importantly, the total amount of oil that will be dispersed as OPAs are highly dependent on a number of variables, which can vary with environmental conditions (e.g., salinity, temperature, and turbulence), the oil properties (e.g., viscosity and polar content), and/or sediment properties (e.g., sediment concentration, hydrophobicity, and particle size) (Gong et al., 2014; Loh et al., 2014; Sun & Zheng, 2009).

4.1.1. Influence of Environmental Conditions on Microscopic Aggregate Formation

Environmental factors such as salinity, turbulence, and temperature can vary both spatially and temporally in nearshore environments. In order to understand the effects of these changes, studies have been carried out to understand the impacts of these factors on OPA formation. One of the most important environmental factors that affect OPA formation is turbulence. The turbulence in a nearshore environment can vary significantly by location and can also vary greatly within a location based on local weather events such as storms. The energy dissipation rate is a key factor that controls the formation of OPAs, because it facilitates mixing by breaking down an oil slick into smaller droplets and also keeps fine sediments in suspension (Sun et al., 2014). Typical values of energy dissipation rate per unit volume for breaking waves can be up to 8 orders of magnitude higher than in the deep sea, which is why OPA formation is typically seen in nearshore environments, as opposed to in the open ocean (Delvigne & Sweeney, 1988). For example, in the years following the Deepwater Horizon oil spill, Adhikari et al. (2015) found that concentrations of hydrocarbons attached to particulate matter (including both OPAs and marine oil snow) were 1–2 orders of magnitude lower in the open ocean than in nearshore waters. In environments with high mixing energy, OPA formation will be more efficient and will occur more rapidly than in calmer environments (Devadoss et al., 2009; Sun et al., 2010; Sun et al., 2014). Additionally, at higher mixing energies, the droplets trapped in OPAs 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 OPA formation. Droplet stabilization in OPAs occurs relatively fast, typically taking less than 24 h, and often occurring within 1–3 h under laboratory conditions (Hill et al., 2002; Ma et al., 2008; Sun

et al., 2010). Several studies have shown that the amount of oil dispersed as OPAs rapidly increases initially, but levels out over time (Payne et al., 2003; Sun et al., 2010, 2014). Ma et al. (2008) conducted mixing experiments to demonstrate that once formed, OPAs tend to be stable, and can withstand continued exposure to turbulent conditions. However, Zhao et al. (2017) recently found that under turbulent conditions, the droplets in OPAs will continuously break apart, resulting in smaller droplets which then recombine to form larger OPAs composed of many small droplets. They demonstrated that these multiple-droplet OPA clusters could persist even after 48 h of continued turbulence. It should be noted that these mixing energy studies were all performed under laboratory conditions; however, the turbulence generated within the baffled flasks, used by studies such as Ma et al. (2008), is simulated to closely resemble the turbulence caused by breaking waves.

The salinity of water can vary seasonally and spatially in nearshore environments, especially when there is a nearby discharge from a freshwater source. Studies have shown that when oil is spilled in a freshwater system that discharges to the ocean, the potential to form OPAs can vary at different points as the oil is transported to increasingly saline conditions (Miranda et al., 2016). OPA formation will rapidly increase as salinity increases until a critical salinity value is reached, after which OPA formation will level off; this critical salinity value is dependent on the type of oil and sediment present (Khelifa et al., 2003, 2005; Le Floch et al., 2002). This critical salinity value might be as low as 0.15 g/L (Le Floch et al., 2002) or as high as 35 g/L (Khelifa et al., 2005) depending on oil and sediment properties. This demonstrates why OPA formation is more effective in marine environments than in freshwater environments, although OPAs have been shown to form in both systems (Fitzpatrick et al., 2015).

Temperature distribution at a spill site can vary greatly depending on the location and the season in which a spill occurs. OPA formation decreases with decreasing temperatures and can be significantly limited in colder environments (Lee et al., 2012; Stoffyn-Egli & Lee, 2002); additionally, the size of OPAs increases with decreasing temperature (Wang et al., 2013). Temperature affects OPA formation because it influences the viscosity and adhesion properties of oil, which control the oil's ability to break into small droplets (Danchuk & Willson, 2011; Delvigne, 1987; Khelifa et al., 2002; Liu et al., 2006). Although OPAs form more readily under warmer conditions, they still form in significant quantities under low-temperature conditions, which have led to recent research into the intentional formation of OPAs for remediating arctic oil spills (Lee et al., 2011, 2012; Wang et al., 2013). These studies are discussed further in our remediation section.

4.1.2. Influence of Oil Type on Microscopic Aggregate Formation

Different types of oil are unique in both chemical composition and physical properties, and these characteristics can significantly impact OPA formation processes. The viscosity of oil positively correlates with the ability of that oil to disperse into microscopic droplets (Delvigne & Sweeney, 1988). Since small droplets are necessary for OPA formation, increasing viscosity can result in a decrease in an oil's ability to form OPAs (Kepkay et al., 2002; Khelifa et al., 2002; Omotoso et al., 2002; Stoffyn-Egli & 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 OPA formation (Bragg & Yang, 1995; Guyomarch et al., 2002; Sørensen et al., 2014). However, oils with higher polar content tend to have higher viscosities, which can complicate predictions of OPA formation. Khelifa et al. (2002) developed an empirical approach for modeling the coupled effects of changes in viscosity and asphaltene content on the amount of oil that could be stabilized within OPAs.

Chemical and physical oil properties vary not just between types of oil but also between weathering stages for a single type of oil. Weathering processes such as evaporation, photodegradation, dissolution, biodegradation, and emulsification begin immediately following the release of an oil into the marine environment and result in changes in the properties of the spilled oil over time. As lighter components leave the oil matrix, the overall viscosity and polar content of the oil will increase. Gustitus et al. (2017) demonstrated that as oil weathers, the oil's propensity to form OPAs can decrease significantly, suggesting that the negative effects of physical changes such as increased viscosity on OPA formation are greater than the positive effects of chemical changes such as increased polar content. Additionally, this study showed that even after several days of intense weathering, a significant amount of lighter crude oil could still be partitioned into OPAs, whereas after only 1 or 2 days of intense weathering, the amount of heavy crude oil that formed OPAs dropped precipitously.

4.1.3. Influence of Sediment Type on Microscopic Aggregate Formation

In addition to variables related to the oil type and environment, the type, size, and concentration of sediment can vary greatly between different oil spill scenarios and nearshore environments and will affect the formation of OPAs. Several studies have shown that OPA formation will increase with increasing sediment concentrations, at least until the concentrations of oil and sediment reach near equivalence, at which point OPA formation tends to reach its maximum efficiency (Ajijolaiya et al., 2006; Khelifa et al., 2007, 2008; Sun et al., 2010). However, this observation is based on laboratory studies, where it is easy to determine oil concentration as a ratio of a known volume of oil to a known volume of water. Conversely, in real-world situations the volume of water interacting with a spill cannot be easily estimated, as in a closed container where it can be quantified, making it impossible to determine an accurate oil concentration. In addition to the concentration of sediment, the type of sediment also influences OPA formation. Studies have shown that the amount of OPAs that can be formed is inversely proportional to sediment particle size (Ajijolaiya et al., 2006; Poirier & Thiel, 1941; Zhang et al., 2010). The amount and type of suspended sediment affect not only the amount of oil trapped in OPAs but also the size and type of OPAs that are formed (Cloutier et al., 2003; Guyomarch et al., 2002; Omotoso et al., 2002; Stoffyn-Egli & Lee, 2002). For example, O'Laughlin et al. (2017) observed that an increase in sediment concentration corresponded to an increase in OPA size and Stoffyn-Egli and Lee (2002) observed that by varying the sediment type they could produce either droplet, solid, or flake OPAs.

Recent studies have sought to identify the most effective sediment for OPA formation. Kaolinite has long been recognized as one of the most effective natural minerals for OPA formation (Poirier & 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 to be effective. Clays are more effective than other minerals, such as quartz, in part because of they have higher surface area (Omotoso et al., 2002; Zhang et al., 2010). Additionally, hydrophobic minerals have a greater tendency to form OPAs 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 that sediment type and content can have an impact on OPA formation, and therefore, their effects should be considered when attempting to predict OPA formation in a nearshore environment.

4.1.4. Transport of Microscopic Aggregates

Several researchers have attempted to create computer models that can generate robust predictions of OPA formation and transport. Early models utilized inputs such as oil content, sediment load, and environmental conditions and focused on simulating the amount of OPAs that will form (Bandara et al., 2011; Danchuk & Willson, 2011; Khelifa et al., 2005; Sterling et al., 2004). The recently developed A-DROP model has the capability to predict the amount of oil trapped in OPAs (Zhao et al., 2016). This model uses a new conceptual framework for predicting oil-particle coagulation efficiency, which is based on an improved version of other established methods (Bandara et al., 2011; Hill et al., 2002; Sterling et al., 2004) that are used to model 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 model oil interactions with either organic or inorganic particles. The A-DROP model has been used to model experimental observations, and it has also been used to simulate expected oil-sediment interactions in a hypothetical "sediment-rich" nearshore environment. The model, however, lacks integration of key coastal dynamics, such as strong currents and sediment transport, which can significantly influence OPA formation and transport processes.

Although the formation of microscopic aggregates is desirable because OPAs are easily dispersed and thereby reducing the amount of oil that is retained on beaches (Ajijolaiya et al., 2007), there is still some concern that OPAs can accumulate in benthic sediments where they may affect various bottom-dwelling organisms (Niu et al., 2010, 2011). A modeling study by Niu et al. (2014) compared scenarios where oil spilled in arctic waters was exposed to turbulence either with or without the addition of mineral fines. They found that after 5 days, oil dispersed without mineral fines remained primarily at the water surface, while of the oil dispersed with the addition of minerals, up to 21.3% accumulated in bottom sediments and up to 32.6% remained in the water column.

As part of the Svalbard trials, observations of oil accumulation in bottom sediments were made following the cleansing of an experimentally oiled beach plot by OPA formation (Lee et al., 2003). At two experimental plots, residual oil concentrations in surface sediments were found to increase with increasing distance from the shoreline, and also the concentrations were higher 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. It has been well established that as the mixing energy decreases, OPAs and other fine particles will settle at higher rates (Lee et al., 2003; Niu et al., 2011). Modeling studies have shown that over time, currents will push settled OPAs out of the initial deposition area, gradually decreasing the amount of oil accumulated in bottom sediments near the shore, while wave action reduces the initial rate of oil deposition by continuously suspending OPAs back into the water column (Niu et al., 2011). Additionally, OPAs are less likely to settle when they are formed in environments with smaller sediment particle sizes or lower concentrations of suspended matter (Niu et al., 2011, 2014).

4.2. Formation of Macroscopic Agglomerates

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 SOAs and SOMs, are lacking (Warnock et al., 2015). Michel and Galt (1995) is one of the first studies that systematically documented some of the rare incidences of SOA and SOM formation resulting from various spills across the globe. The Bouchard 155 spill that affected Tampa, FL, in August 1993, released a dense and viscous fuel oil that readily mixed with sediment and sank. This resulted in several patches of SOMs and SOAs that were difficult to find as they transported and/or buried within the bottom sediment. Action was taken only to remove pieces of these agglomerates 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 offshore 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 as SOMs; however, each day some of this oil separated from the mats and reemerged to form a slick at the surface (Burns 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 SOAs, which were deposited in the intertidal zone and became buried when calm poststorm conditions transported sediment from the subtidal to the intertidal zone (Bernabeu et al., 2006). SOAs have also been deposited over several years along the west coast of India; source identification studies have revealed that most of the SOAs that were deposited along the western coast of India in 2010 originated from residues discharged by oil tankers traveling nearby, while the SOAs that were deposited from 2012–2014 originated from the Bombay High oil fields (Suneel et al., 2014, 2015, 2016).

Although SOAs and SOMs have resulted from several spills in the past, they were recently brought into the spotlight following the Deepwater Horizon oil spill, which resulted in a large amount of SOAs and SOMs that continue to affect the Gulf of Mexico beaches to date (Clement et al., 2017; Hayworth et al., 2015; Nixon et al., 2016). Figure 6 shows a conceptual model describing the process that led to the formation of SOMs and SOAs near sandy beaches based on observations following this spill (OSAT-2, 2011; OSAT-3, 2013). Unlike OPAs, which can form from both fresh or weathered oil, but are more likely to form from fresh oil (Gustitus et al., 2017), SOAs 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 SOAs to form, the coastal dynamics must facilitate the interaction of coarse sediment with mousse through a three-step process (Clement et al., 2017; OSAT-3, 2013). Typically, the first step occurs either near a sandbar or in the swash zone where breaking waves force sediments to interact with the floating oil (see Step 1 in Figure 6). After accumulating a sufficient amount of sediment, the density of the sediment-mousse mixture will increase, causing it to sink (see Step 2 in Figure 6). Once the mass has reached the seafloor, the sunken mixture may accumulate additional sediment, forming SOAs and SOMs (see Step 3 in Figure 6). However, unlike OPAs, which are typically stable once formed, SOAs and SOMs can change shape or break apart into smaller pieces when exposed to continued turbulent conditions (Dalyander et al., 2014; OSAT-2, 2011).

4.2.1. Physical Characteristics of Macroscopic Agglomerates

Due to the magnitude of SOA and SOM contamination along the northern Gulf coast following the Deepwater Horizon spill, several studies have been carried out to understand the distribution, transport

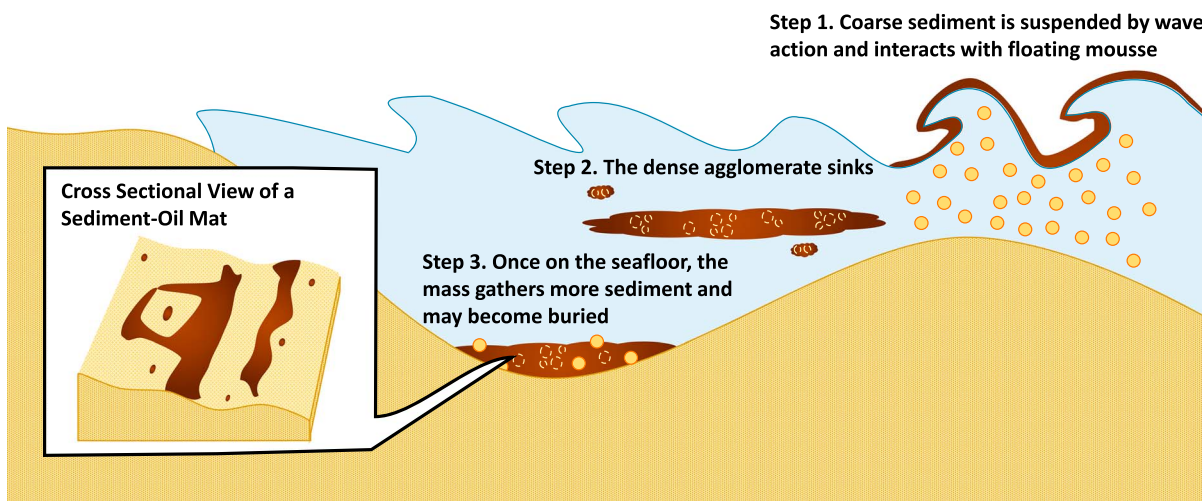


Figure 6. Conceptual model of the formation of macroscopic agglomerates when oil and sediment interact near a sandbar. Macroscopic agglomerates may also form when oil and sediment interact in the swash zone (not pictured).

dynamics, and physical and chemical characteristics of these agglomerates, 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 & Roberts, 2013; Yin et al., 2015), and some in Florida (Wang & Roberts, 2013). SOAs 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 & Huettel, 2016; Hayworth et al., 2015; Michel et al., 2013). Field observations of SOAs and SOMs revealed that these aggregates were formed with 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 are typically found either atop the sediment layer, buried within the sediment, or washed up to rest in the supratidal zone (Dalyander et al., 2014; OSAT-2, 2011; OSAT-3, 2013; Plant et al., 2013). SOAs are often referred to colloquially as tar balls; however, in contrast to traditional pelagic tar balls, which are rubbery with little or no sediment incorporated, SOAs are a type of benthic agglomerates that have sand and/or clay not only on the outer surface but also throughout the interior (Hayworth et al., 2015). The SOAs and SOMs collected following the Deepwater Horizon spill had a high characteristic sand content ranging from about 83 to 97% by mass (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 & Galt, 1995; Warnock et al., 2015), and therefore, the majority of benthic oil residues that are found in the nearshore environment are either SOAs or SOMs.

There is also a specific subclass of SOAs, identified here as onshore-SOAs. The onshore-SOAs are formed when beached mousse is later buried under dry sand transported by wind, or partially wet sand deposited by storm surges. Figure 7a shows an example of an onshore-SOA found in Orange Beach, Alabama, about 5 months after the Deepwater Horizon oil spill. Typically, these onshore-SOAs are rather fragile agglomerates of oil and dry sand and can be easily broken apart and smeared into an oily layer (Hayworth et al., 2011), such as the one shown in Figure 7b. The in situ response of indigenous bacterial communities to the residual oil trapped in one of the onshore-SOAs, which was found along Pensacola beach in Florida, has been studied extensively (Kostka et al., 2011; Rodriguez-R et al., 2015). The 2011 study concluded that the Deepwater Horizon (DWH) spill altered the abundance and community composition of indigenous bacteria in beach sands, and a few selective populations became the key players in degrading the buried oil. The Rodriguez-R et al. (2015) study showed that at the latter time point, a typical beach community had reestablished that showed little to no evidence of oil hydrocarbon degradation potential; however, the community was different from the one that existed prior to the DWH oil spill.

Based on field observations, it is accepted that in order to form SOAs and SOMs of benthic origin, the oil must undergo sufficient weathering, including the emulsification process, before it is subjected to turbulent

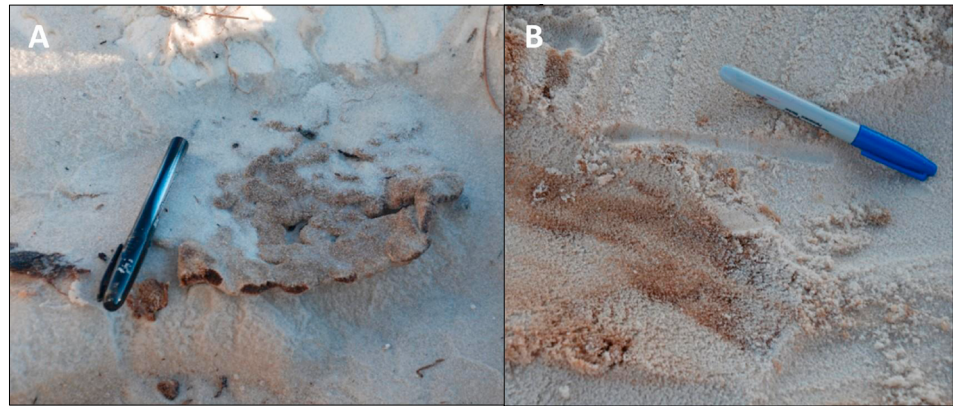


Figure 7. Examples of an (a) intact onshore-SOA and (b) an oily layer that was produced when an onshore-SOA was broken down. These residues were a result of the Deepwater Horizon oil spill.

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 SOAs and SOMs (OSAT-2, 2011). Interestingly, in contrast to the plethora of lab studies that have been carried out to understand the formation dynamics of OPAs, there has been a dearth of lab work done to better understand the variables that affect SOA and SOM formation. 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 2 months. All of the tar balls produced in the study were buoyant, except for one that 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; however, no information was derived on their physical properties or the dynamics involved in their formation. Lee et al. (1989) observed in their 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 SOAs. 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 SOAs and SOMs of benthic origin.

4.2.2. Transport of Macroscopic Agglomerates

Buried SOAs and SOMs are particularly challenging to remediation teams because they can be difficult to find and can reappear along the shorelines of 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 SOAs can be continuously formed by the fragmentation of SOMs, a dense accumulation of SOAs on a shoreline can be indicative of the presence of a large SOM in the nearby surf zone (OSAT-2, 2011). Figure 8 shows deposition patterns of SOAs on the shore adjacent to a SOM that remains submerged. Angular SOAs are believed to be recently broken pieces of larger SOMs, while rounded SOAs 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 SOAs can be found in the subtidal, intertidal, or supratidal zones (OSAT-3, 2013) (Figure 9).

Numerical modeling tools have been used to better understand and predict the causes, hindrances, and patterns of the mobility of



Figure 8. Sediment-oil agglomerates (SOAs) accumulated on the shoreline next to a sediment-oil mat (SOM) resulting from the Deepwater Horizon oil spill. Adapted from John et al., 2016.

Deepwater Horizon SOAs along the Alabama/Florida coast based on different currents and wave conditions (Dalyander et al., 2014; OSAT-3, 2013; Plant et al., 2013). The various shoreline conditions were used to account for changes in wave height, direction, and period, as well as wind speed and direction. In order to determine SOA mobility, this study compared the shear stress created by the coastal conditions with critical threshold values of incipient motion for SOAs. Modeling results revealed that while SOAs that are atop the seabed are mobile approximately 60% of the time, SOAs that are buried are unlikely to be mobilized under most hydrodynamic conditions. Additionally, the results showed that wave heights can play a significant role in shoreline contamination, with SOAs being mobile in small patches of the coastline 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 SOAs larger than 2.5 cm in diameter will be relocated under normal conditions and will most likely be buried and exhumed periodically in the same location. However, storm events may uncover and redistribute larger SOAs up to 10 cm in diameter. Modeling studies have also revealed that coastal inlets accumulate SOAs in greater quantities than other shoreline features (Dalyander et al., 2014; Plant et al., 2013). These results were verified by field observations of SOA distributions by Dalyander et al. (2014). In order to further verify the results of this study, Dalyander et al. (2015) generated artificial SOAs 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 best suited for predicting the movement of SOAs present on the surface of the seabed. Additionally, the largest artificial SOA (10 cm diameter, of ellipsoidal shape) became buried after 10 min at a depth of 0.5 m, confirming the importance of accounting for burial and exhumation processes when predicting SOA mobility. It is hypothesized that the highest estimations of critical stress from the models are appropriate for partially buried SOAs (Dalyander et al., 2014; Plant et al., 2013), but this was not confirmed by this study because the movement of buried SOAs was not observed. These studies have provided key insight into understanding the movement of SOAs, but the movement and breakdown of SOMs are still not well understood. Since SOMs are the primary source of continual SOA contamination, additional research in this area is warranted.

4.3. Lessons Learned From Reviewing the Formation and Transport Processes of Microscopic Aggregates and Macroscopic Agglomerates

Microscopic aggregates have been studied in depth, allowing the microscopic community to develop a detailed understanding of how environmental, oil, and sediment variables affect the formation of these aggregates. However, macroscopic agglomerates have not been studied in nearly as much depth, and hence, we only have a limited understanding of how the same variables affect the formation of SOAs and SOMs. Since the basic components of microscopic and macroscopic oil-sediment residues are the same (oil and sediment), it is reasonable to expect that the variables that affect the formation of microscopic aggregates would also affect macroscopic agglomerate formation, albeit not necessarily to the same extent. For example, there have been several studies on how mixing energy affects the rate and degree of OPA formation (Ma et al., 2008; Payne et al., 2003; Sun et al., 2010, 2014); however, beyond the conceptual idea that breaking waves facilitate SOA and SOM formation, there is no consensus in the macroscopic community about how more turbulent nearshore environments might affect macroscopic agglomerate formation. Similarly, several studies have been carried out to understand how the likelihood of OPA formation differs for different types of oils (Gustitus et al., 2017; Guyomarch et al., 2002; Kepkay et al., 2002; Khelifa et al., 2002; Omotoso et al., 2002; Sørensen et al., 2014; Stoffyn-Egli & Lee, 2002); however, the macroscopic community has not carried out any such controlled studies, although it could be assumed that oil qualities such as density, polarity, and viscosity would have a significant impact on macroscopic agglomerate formation. Therefore, we believe that the macroscopic community should gain an understanding of the work that has already been completed by the microscopic community and use it to design comprehensive laboratory studies to explore the effects of environmental, oil, and sediment variables on SOA and SOM formation. By developing an understanding of the variables that affect macroscopic agglomerate formation, it may become possible to predict which spill scenarios pose the highest risk of SOA and SOM formation. This information can provide remediation team guidance for taking preventative measures to mitigate the negative impacts of macroscopic agglomerates. Additionally, since nearshore environments are conducive to the formation of both microscopic aggregates and macroscopic agglomerates, it is recommended that further field research be done to explore which conditions are more favorable to the formation of each type of aggregate.

Improving our current understanding of the formation of both microscopic and macroscopic oil-sediment residues can help improve oil spill budget calculations that account for the fate of oil that is released from an accidental spill. A study by Niu et al. (2014) used numerical modeling to predict oil budgets for several hypothetical scenarios built around the field experiments completed by Lee et al. (2011). These model-based calculations indicated that within 12 h after the application of mineral fines to the slick dispersed about 43% of the oil into the water column as OPAs. While this study also predicted the amount of oil that would reach the shoreline, it did not differentiate the forms of oil that could be deposited near the shoreline. As per our knowledge, currently, there are no field or large-scale laboratory studies available that have quantified the amount of oil distributed in the form of OPAs or SOAs/SOMs following a spill. In real-world situations, typically, the amount of oil trapped in these forms are lumped under a generic category, such as “dispersed” or “other.” For example, the budget for the Deepwater Horizon oil spill reported that 41% of the oil was removed by human interventions at sea, 24% of the oil evaporated or dissolved, and 13% of the oil was naturally dispersed through mechanisms that could have included OPA formation, while 22% of the oil fell in the “other” category, which includes oil trapped as SOAs and SOMs, collected from shoreline remediation efforts, ingested by microbes, and/or remaining in the water column (Ramseur, 2010). Since accurate quantification methods to estimate the amount of OPAs, SOAs and SOMs formed following an oil spill are currently not available, we recommend that both microscopic aggregate and macroscopic agglomerate researchers should engage in joint field and large-scale laboratory research efforts to develop rigorous tools that can help quantify these residues. This is an excellent opportunity for collaborative efforts between the two groups.

5. Fate

5.1. 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. 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 OPAs clearly facilitates rapid biodegradation, while the formation of SOAs and SOMs inhibits biodegradation, and thus can hinder the weathering of toxic components trapped in oil spill residues.

5.1.1. Weathering of Oil in Microscopic Aggregates

The formation of OPAs can help facilitate natural dispersion as well as oil biodegradation processes, and there are two main mechanisms that make this possible. First, oil that is trapped in OPAs is in the form of micrometer-scale droplets and is less likely to re-coalesce with the surface slick or adhere to shoreline materials, thus increasing its overall available surface area (Bragg & Yang, 1995; Jahns et al., 1991; Owens, 1999). Second, OPA-entrained oil is associated with suspended particulates that typically host greater numbers of microbes than the surrounding water (Harvey & 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 & Young, 1980; Hendricks, 1974; Kirchman & Mitchell, 1982).

Lab studies have demonstrated that OPA formation both increases and accelerates 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 1 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 2 months, despite the low temperatures in the ice-infested waters where the study was conducted. Furthermore, it has been posited that while the incorporation of oil into OPAs enhances the accessibility to the oil by microorganisms, it also reduces the bioavailability and toxicity of the oil to larger aquatic organisms (Fitzpatrick et al., 2015). Most recently, field samples that were analyzed following the Deepwater Horizon oil spill showed that levels of particulate-bound polycyclic aromatic hydrocarbons (PAHs) and alkanes decreased significantly in surface waters from 2010 to 2011. This reduction was credited to weathering processes, including dilution and biodegradation, which were facilitated by the interaction of oil and particulate matter (Liu et al., 2016).

5.1.2. Weathering of Oil in Macroscopic Agglomerates

Unlike the formation of OPAs, which enhances oil biodegradation rates, the formation of SOAs and SOMs can significantly hinder oil degradation (Pendergraft & Rosenheim, 2014). Because of this, oil trapped in SOMs and SOAs may persist in the environment for years following a spill. Published studies have documented the persistence of SOAs up to 9 years after the Prestige oil spill (Bernabeu et al., 2013) and 6 years after the Deepwater Horizon oil spill (Clement et al., 2017). Typically, the oil that forms SOAs 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 PAHs (Liu et al., 2012; Stout et al., 2016). Therefore, the oil that is derived from macroscopic agglomerates will always show reductions in alkanes, saturates, and PAHs compared to fresh oil; however, the reductions in the rate of degradation of these compounds once they are trapped in SOAs and SOMs have been a major concern (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).

The persistence of toxic PAHs within SOAs 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 SOA 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% when the oil transported over the surface of the Gulf of Mexico. Specifically, various light PAHs, such as naphthalenes were fully depleted, while heavy PAHs, such as chrysenes, were only partially depleted. By comparing the SOAs 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, indicating that PAH weathering rates decreased significantly once the mousse was buried as SOAs and SOMs. Their study postulated that evaporation was most likely the primary weathering mechanism that weathered lighter PAHs, followed by photodegradation that also weathered heavy PAHs. A later study demonstrated how the burial of SOMs and SOAs would have hindered sunlight exposure and hence inhibited photodegradation (John et al., 2016). Experimental results of 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 reexposed to sunlight, the weathering reactions were reactivated, indicating that when natural processes fragment SOMs and reexpose them to sunlight, the photodegradation reactions will indeed degrade heavy PAHs. The degradation of SOAs and SOMs may be further influenced by the morphodynamic behavior of the afflicted beach, as was seen for SOAs resulting from the Prestige oil spill (Bernabeu et al., 2006; Bernabeu et al., 2009). When these SOAs became buried, the accumulated sediment exerted increased pressure on the residues, eventually breaking them down into smaller pieces. Although the burial inhibited the weathering rates of the SOAs, their fragmentation accelerated the overall rate of other natural remediation process (Bernabeu et al., 2006).

Biodegradation is a major pathway for degrading PAHs trapped in oil spill residues. Simister et al. (2015) isolated fungi from the Ascomycota phylum that were found in Deepwater Horizon SOAs 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) measured PAHs, alkanes, and hopanes in SOAs and SOMs 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, while SOAs 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 of oil (Elango et al., 2014; Urbano et al., 2013). In contrast, oil-degrading microbes in supratidal SOAs benefit from aerobic conditions and higher (albeit, still relatively low) nutrient levels than SOMs, especially SOAs in the intertidal zone, which are regularly inundated with seawater containing nitrogen (Elango et al., 2014). This study also demonstrated that PAH degradation was limited in regions of hypersaline conditions but was higher in supratidal SOAs 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 they also observed no significant changes in chrysene concentrations. These studies have indicated that heavy PAHs, such as chrysene and its alkylated homologs, could remain trapped in SOMs and SOAs for several 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 SOAs over time (Aeppli et al., 2012; Huba & Gardinali, 2016). A study by Aeppli et al. (2012) analyzed SOAs 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 by White et al. (2016), and they also identified that these compounds continue to accumulate over time. OxHCs are recalcitrant once formed, and they are difficult to quantify using standard analytical techniques. Much like heavy PAHs, OxHCs are expected to persist in the environment for many years, and currently, we do not fully understand the long-term impacts of these oxygenated compounds.

5.2. Remediation

The goal of any remediation effort is to minimize the environmental impacts, either by physically removing or by rapidly dispersing and degrading the oil before it can cause harm to the environment. The formation of OPAs aids both dispersion and degradation processes, while the formation of SOAs and SOMs hinders these processes. Therefore, in recent years, remediation engineers have attempted to develop cost-effective strategies to enhance OPA formation in order to disperse and degrade large quantities of oil (Ajijolaiya et al., 2007). Conversely, remediation engineers are primarily concerned with the negative impacts of SOA and SOM formation and have sought ways to safely and efficiently remove these residues from the environment.

5.2.1. Remediation of Oil Spills by Enhancing Microscopic Aggregate Formation

The cost-effectiveness and environmental friendliness of dispersion through OPA formation have led to the desire to facilitate this process through human intervention to speed up oil spill remediation. This is accomplished by using either one of the following two methods: (1) moving contaminated sediment from the high tide zone down to the surf zone to enhance OPA formation in a process known as “surf washing” or (2) applying a sediment slurry directly to an oil slick to enhance OPA formation.

5.2.1.1. Surf Washing

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. The wave action in the surf zone releases 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 OPAs. 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 the removal of a visual oil stain from the sediment after one to two wave cycles (Owens et al., 1995). Surf washing was also utilized in response to the Sea Empress oil spill in 1996; in this case, sediment relocation resulted in the removal of the majority of beached oil after 4 days of treatment (Lee et al., 1997). During this study, OPA formation resulting from the surf washing efforts was verified, for the first time, using 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 compared to natural attenuation and to obtain further microscopic observational data for OPA formation (Lee et al., 2003; Sergy et al., 2003). These studies have demonstrated that surf washing can greatly accelerate natural OPA formation and can help reduce the amount of residual oil trapped in the shoreline system.

5.2.1.2. Sediment Slurry Application

Some studies have suggested that OPA formation can be facilitated by directly applying a fine sediment slurry to an oil slick (Bragg & 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 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 boat propellers. As a result, the oil was rapidly dispersed into the water column, with minimal resurfacing. Additionally, microcosms of field samples collected from this study showed that over 56% of the dispersed oil degraded within a 2 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; the addition of the slurry allowed a significant amount of the oil to be dispersed as OPAs into the water column with a lesser amount settling 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 studied in arctic environments, where low temperatures limit the effectiveness of either chemical dispersants or sediment application alone. Chemical dispersants led to increased oil concentrations and decreased sizes of oil droplets in the water column, and this promoted interactions between oil and fine minerals, thereby facilitating OPA formation (Khelifa et al., 2008; Li et al., 2007). The combined presence of chemical dispersants and mineral fines can lead to more effective dispersion of oil than when either chemical dispersants or mineral fines are present alone; therefore, this has been shown to be a promising remediation approach (Lee et al., 2012; Li et al., 2007; Wang et al., 2013). In a bench-scale study simulating oil spills in low temperature (0–4°C) environments, Wang et al. (2013) treated three different oils with combinations of kaolinite and chemical dispersant in various ratios. The study 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 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 not been tested in response to an actual oil spill.

5.2.2. Remediation of Oiled Shorelines Through Removal of Macroscopic Agglomerates

Remediation procedures concerning SOAs and SOMs differ greatly from those concerning OPAs. While remediation teams seek to enhance OPA formation, they typically seek to prevent SOA and SOM formation and try to remove them quickly when they do form. From an economic standpoint, removal of SOMs and SOAs is especially important when they are formed near pristine amenity beaches, since they could greatly affect the local tourism industry (Cirer-Costa, 2015; Clement et al., 2017). Currently, the only way to avoid the formation of SOAs and SOMs near sandy beaches is to prevent the oil from reaching the shoreline. Since this is often impossible, the remediation teams must resort to removing these residues after they have formed.

In order to remediate SOA and SOM contamination, the location of the agglomerates and the extent of contamination must first be identified. Visual and aerial inspections may be used to assess surface contamination (such as supratidal SOAs and intertidal SOAs and SOMs) that needs to be removed. Sediment cores or trenches are used to assess and remove subsurface contamination such as beach-SOAs (OSAT-3, 2013). During investigation, it is important to use an appropriate subsurface excavation technique 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. Following the Deepwater Horizon oil spill, trenches that were several meters long were used to locate subsurface SOMs and SOAs as part of the Buried Oil Project (OSAT-3, 2013). During beach characterization efforts, workers directly cored the dry beach all the way to the water table using small auger drills. Coring and trenching are effective methods for identifying large deposits of onshore-SOAs and SOAs that have washed ashore and later buried under dry beaches. Unfortunately, most SOAs and SOMs are formed when the oil is submerged under several meters of water and eventually buried under a benthic sediment layer; these residues are almost impossible to detect (Michel et al., 2013). Also, these mobile macroscopic agglomerates can be periodically exhumed and/or transported by coastal processes, making discovery by aerial observations difficult. Newer methods to identify and remove submerged oil such as sonar or fluorometry have been explored, but they are not yet 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 SOAs (which are recently fragmented SOMs) along the waterline to indirectly assess possible SOM locations (Dalyander et al., 2014; Hayworth et al., 2015; OSAT-2, 2011).

After the Deepwater Horizon oil spill accident, BP's remediation team completed Operation Deep Clean (ODC) to clean contaminated beaches. During this effort, the presence of onshore-SOA contamination was identified by sediment cores or trenches, and the contaminated region was excavated within a 150 m² area around the core location all the way to a depth of about 2 to 4 m (close to the water table boundary). The excavated sand was filtered through mechanical sifters, which were shown to achieve in 80–95% recovery rates from a single pass (Owens et al., 2011). These machines sieved the surface layer of contaminated sediment through a screen where the fine material (sand) was separated and returned to the beach, while the large oil-sand aggregates were retained and transferred to a debris hopper (Owens et al., 2011). Figure 9 shows some excavation and mechanical cleaning operations completed during the ODC efforts. While ODC was indeed effective in treating large volumes of contaminated sand, these mechanical sifters could

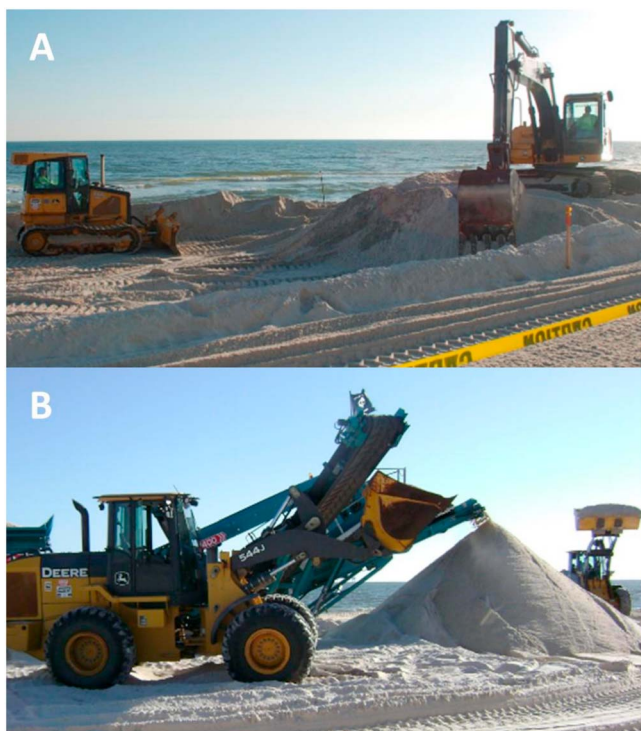


Figure 9. Sediment contaminated by SOAs from the Deepwater Horizon oil spill being (a) excavated and then (b) sifted and returned to the beach.

not remove all of the oil contamination (Hayworth & Clement, 2011; OSAT-2, 2011; Owens et al., 2011). An observational study by Hayworth and Clement (2011) indicated that the sifting process removed all solid matrix constituents such as shells, marine debris, along with the chunks of consolidated oil-sand agglomerates. The process also broke some of the softer oil-sand agglomerates into smaller fragments, which were then mixed with the sand passing through the sieve.

It is important to note that the use of sifting and tilling processes is limited to removing onshore-SOAs or benthic SOAs that are beached and buried under dry sand. The removal of SOMs, which are submerged oil buried offshore, requires the use of long-arm excavators that can be driven into the swash zone to excavate larger patches of SOMs (Hayworth et al., 2011). Buried SOMs are occasionally exposed by natural sediment transport processes, and whenever they can be located, it is desirable to immediately remove these mats of oil. However, removal of SOM deposits is typically limited by the reach of a standard long-arm excavator (which is about 20 m; see Figure 10a). It is also limited by the depth at which these excavators can operate (which is a maximum of about 2 m of water depth). This presents a serious challenge for removing SOMs that might have formed and buried near sandbars that are up to 500 m away from the shoreline. Currently, we simply do not have any technological solution to address this problem.

Neither sifting contaminated beaches nor excavating SOMs can remove the many centimeter-scale SOAs that can be distributed over a large span of time along the intertidal and subtidal zones (OSAT-3, 2013). No mechanical methods are currently available to remove these SOAs, which are commonly intermingled with other macroscopic marine matter such as shells (Figure 11). Cleanup crews are often deployed to manually collecting these SOAs (Hayworth et al., 2015). Figure 10b shows a typical BP cleanup crew manually removing SOAs from the Alabama shoreline in February 2013, 3 years after the spill. The effectiveness of this manual cleanup procedure is currently unclear since the manual operations are typically terminated once certain “cleanup goals” are assumed to be met. However, a rational basis for developing these goals is difficult to establish a priori, and the residues might continue to wash ashore for many years after terminating all cleanup activities. For example, after the Deepwater Horizon oil spill, the manual cleanup operations were terminated in June 2013, claiming that the cleanup goals were satisfied. However, Clement et al. (2017) study recently pointed out that as of January 2016, large amounts of SOAs continue to be actively deposited on various Alabama beaches, increasing background oil contamination levels by up to 4 orders of magnitude. The remnant SOA deposition level can have seasonal



Figure 10. (a) An excavator removes a submerged SOM that resulted from the Deepwater Horizon oil spill. (b) A team of volunteers collects SOAs along the shoreline.



Figure 11. Sediment-oil agglomerates (SOAs) indicated by red circles that are deposited with shells on a beach following the Deepwater Horizon oil spill.

variations and may become particularly pervasive following large storm events (Hayworth et al., 2015; Plant et al., 2013); however, the contamination levels will generally decline over time (Dalyander et al., 2014). More monitoring studies are needed to fully understand the long-term fate of SOMs and SOAs formed from large oil spill events, and their impacts on oil background levels.

More recently, researchers have published studies that explored methods for intentionally sinking spilled oil. Abkarian et al. (2013) recommended applying dry sediment to directly sink an oil slick as large (millimeter-scale) oil droplets covered in coarse sediment particles. These aggregates are referred to as either “armored droplets” (Abkarian et al., 2013), or “particle-oil aggregates” (Boglaïenko & Tansel, 2015). Bench-scale studies have demonstrated that by applying dry sediment to the surface of a fresh crude oil slick, up to ~95% of the oil can be submerged as armored droplets (Boglaïenko & Tansel, 2015). Follow-up studies demonstrated that the surface porosity and grain size of the dry sediment (Boglaïenko & Tansel, 2016a), as well as the presence of chemical dispersant, can affect the amount of oil that can be submerged using this technique (Boglaïenko & Tansel, 2016b). Boglaïenko and Tansel (2016a) argued that engineered formation of armored droplets does not eliminate the toxic compounds from being released to the environment but reduces their mobility (i.e., keeps the impact radius small) and prevents direct contamination of beaches, birds, and coastal flora. However, it is unclear how the sinking of fresh oil would impact benthic organisms. Sinking fresh oil immediately after the spill will prevent key processes such as evaporation and photodegradation that can rapidly weather the crude oil. These processes can remove a significant amount of oil and toxic compounds such as benzene, toluene, ethylbenzene, and xylenes and lighter PAHs. Additionally, the U.S. Environmental Protection Agency has explicitly banned the use of sinking agents for oil spill remediation according to 40 CFR §§ 300.310(b) and 300.910(e).

5.3. Lessons Learned From Reviewing the Fate of Microscopic Aggregates and Macroscopic Agglomerates

Studies that have been published by the microscopic community often quantify the amount of oil that becomes captured/dispersed as microscopic OPAs, but any mention of the fate of the oil that is not incorporated into OPAs is virtually nonexistent. It is important that the fate of this oil be considered, when recommending the artificial introduction of fine sediment to manage oil spills. Fine sediment can stabilize emulsifications, which are conducive to the formation of macroscopic agglomerates. 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 SOAs/SOMs. Researchers who study microscopic aggregates should develop a better understanding of this sinking process, which can help guide remediation decisions concerning the engineered enhancement of OPA formation. This understanding can also help determine the fate of the undispersed fraction of oil when both fine and coarse sediments are present at a field site.

Fully integrated computer models that can simulate the interaction of floating oil with nearshore sediment transport dynamics are needed to better understand oil sinking processes. An area where research can be improved in both the microscopic and macroscopic communities is characterizing how coastal sediment transport processes would affect oil-sediment interactions. Sandy coasts are highly complex dynamic

systems, and field data collected in the swash and surf zones often reveal the presence of different types of sediment undulations along the shoreline, referred to as morphodynamic patterns (Ribas et al., 2015). These morphodynamic patterns include rhythmic features such as beach cusps, surf zone transverse, crescentic bars, and shoreface-connected sand ridges, which are characterized by different spatial and temporal scales (Ribas et al., 2015). While recent progress is promising, modeling sediment transport processes near beaches continue to remain a formidable challenge (Brocchini & Baldock, 2008). This is because understanding sediment transport processes in coastal systems is an inherently uncertain empirical process, which is compounded by uncertainties arising from turbulence closure schemes (Amoudry & Souza, 2011). However, methods to account for various types of nearshore sediment transport mechanisms in coastal models at different temporal and spatial scales are available in published literature (Amoudry and Souza; Brocchini & Baldock, 2008). The initial interaction of floating oil with suspended sediment, as well as the transport of oil-sediment residues would depend on these sediment transport mechanisms. Therefore, understanding the dynamics of sediment deposition patterns and their short/long-term evolution mechanisms (such as erosion and accretion) is important to develop robust oil spill models that can be used for predicting the fate of both microscopic aggregates and macroscopic agglomerates. These models, which can be developed through close collaboration of oil spill and coastal sediment transport researchers, will serve as useful design tools for planning and managing oil spill remediation activities.

Detecting and removing SOMs buried near coastal environments continues to be an extremely challenging task. Long arm excavators currently used for removing SOMs can only operate close to the shoreline in shallow waters; therefore, better technology solutions are needed to detect and remove SOMs. Finally, one of the most important lessons learned from the remediation of the Deepwater Horizon spill is that sunken oil trapped in the form of SOAs and SOMs will lead to long-term shoreline contamination problems and would result in substantially increasing background oil levels (Clement et al., 2017). Therefore, field-scale monitoring studies are needed to carefully assess the long-term fate of SOAs and SOMs and quantify their adverse impacts on nearshore ecosystems.

6. Impacts

6.1. Environmental and Ecological Impacts of Microscopic Aggregates

Dispersing oil as OPAs has been promoted as a nontoxic alternative to the use of chemical dispersants, which may have potential toxic effects (Chapman et al., 2007; Linden, 1975; Ramachandran et al., 2004). However, the formation of microscopic OPAs 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 OPA formation may affect sensitive organisms, especially in the benthic zone. OPA 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).

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 how enhancing OPA formation through surf washing impacted the toxicity levels of beach sediment, nearshore waters, and nearshore sediment (Lee et al., 2003). 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 sediments 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 sediments 10 days after treatment, and after 61 days there was little difference between the toxicity levels of surf washing and natural attenuation plots. However, based on the guidelines put forth by the Environment Canada, the toxicity levels were not of significant concern at these test sites (Lee et al., 2003).

The results of the toxicity testing on the Svalbard trials support the generally held assertion that dispersion through OPA 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 OPAs under a host of different conditions. Numerical modeling efforts have been used to explore the potential toxic effects of OPAs on benthic organisms (Niu et al., 2010, 2011). Niu et al. (2011) showed that OPA toxicity to benthic organisms is largely dependent on the type of sediment present. Out of the four types of sediments used

in their hypothetical simulation study, only one posed likely risks to benthic organisms. The type and chemical composition of the oil can also significantly alter toxicity risks. Niu et al. (2010) found that the risks associated with aromatic hydrocarbons were greater than those associated with aliphatic groups. This study also demonstrated that the presence of chemical dispersant can increase the amount of oil that is transported to the benthic zone as OPAs, which has been confirmed by other laboratory studies (Cai et al., 2016; Khelifa et al., 2008).

6.2. Environmental and Ecological Impacts of Macroscopic Agglomerates

The risks associated with various forms of unaggregated oil residues (e.g., oil slicks, oil stained sediment, and 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 & Ucan-Marin, 2015) and microorganisms (Kimes et al., 2014; Kostka et al., 2011; Rodriguez-R et al., 2015); however, the ecological impacts of the oil trapped in macroscopic agglomerates are not as well understood (Warnock et al., 2015). Unlike fresh oil, the oil that is found in macroscopic agglomerates typically has lost some (albeit, not all) of its toxic compounds due to weathering. Also, these residues do not present the risk of physically coating or smothering animals living or grazing in benthic waters, like oil slicks do. However, humans and wildlife could still be exposed to SOAs and SOMs through either physical contact or accidental ingestion. As long as aggregates remain on the macroscopic scale, the risk of the oil within them being ingested, inhaled, or absorbed by marine species is minimal. However, the eventual breakdown of macroscopic agglomerates into smaller fragments approaching microscopic aggregate size may increase potential risks by making the oil more mobile and accessible within the water or sediment. For example, sediments contaminated by the Deepwater Horizon oil 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, SOAs 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 & Huettel, 2016).

Understanding the toxicity level of oil spill residues is extremely important because a key factor in any oil spill remediation activity is determining when further remediation, such as the removal of SOAs and SOMs, will do more harm than good to the environment (NOAA, 2000). The shoreline cleanup plans developed for managing the Deepwater Horizon spill took into account the exposure of both humans and wildlife to SOAs almost a year after the spill, as well as the impact of continued remediation efforts on resident species (OSAT-2, 2011; SCCP, 2011). These plans 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 U.S. Environmental Protection Agency (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 SOAs and SOMs would have if they were left in place. The greatest risk that remnant SOAs and SOMs posed to the wildlife considered in this report comes from ingestion of SOAs and SOA 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, studies have shown that SOAs and SOMs have persisted in the near-shore environment, increasing the background oil contamination level by several orders of magnitude (Clement et al., 2017). Additional studies have shown concerns about the toxicity of SOAs, 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 et al., 2014), oxygenated compounds (Aeppli et al., 2012; Huba & 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 that can lead to programmed cell death. The study concluded that SOAs and SOMs have the potential to be toxic to epithelial, kidney, and neuronal cells (Bhattacharya et al., 2016). Wise et al. (2014) detected nickel and chromium, both known human carcinogens and genotoxicants, at levels of 8.5 to 4.8 ppm in SOA samples collected from Florida,

Alabama, and Louisiana beaches. 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 induce toxicity effects (Wise et al., 2014). Kiruri et al. (2013) suggested that EPFRs in large SOAs are not likely to be hazardous because these larger residues are not likely to be inhaled or ingested, but EPFRs in much smaller SOA fragments may pose a risk of cardiopulmonary disease to wildlife species. Tao et al. (2011) suggested that the elevated number of *Vibrio vulnificus* found in SOAs 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 SOAs (Aeppli et al., 2012; Huba & Gardinali, 2016; White et al., 2016) may also present toxic effects since they are more water-soluble and hence are more bioavailable (Charrié-Duhaut et al., 2000).

There have been very few studies concerning the environmental effects of SOAs 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 SOAs from the Prestige oil spill and concluded that the beached SOAs and other residues had minimal effects on the macroinfaunal communities within the first 6 months after the oil spill and had no obvious effects after that. Serrano et al. (2006) surveyed benthic areas affected by macroscopic agglomerates following the Prestige oil spill and found that these aggregates had no significant effects on health indicators for benthic communities. Kalke et al. (1982) studied the effects of weathered oil resulting from the IXTOC I oil spill on estuarine benthic communities in both the laboratory and in situ. 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 9 years after the Haven super tanker spill in the Mediterranean Sea showed that areas with significant amounts of SOAs or SOMs had no noticeable effect on the benthic communities 9 years after the spill (Guidetti et al., 2000). However, the lack of observed toxic effects from the Haven spill could have been due to the 9 year time lag between the spill and the observations, or the fact that the spilled oil was combusted before sinking, and combustion would have removed many toxic compounds.

6.3. Lessons Learned From Reviewing the Environmental Impacts of Microscopic Aggregates and Macroscopic Agglomerates

Several research studies have focused on understanding the toxicity of both microscopic and macroscopic oil-sediment residues. However, an area that could be explored in much greater detail is how the toxicity of macroscopic agglomerates evolves as these agglomerates continuously break down, eventually forming microscopic aggregates. The toxicity research that has been done with regard to OPAs focuses mainly on the concentration of oil that is deposited in bottom sediments because of OPA formation when oil is still relatively fresh. However, this is a different process than the formation of microscopic aggregates from macroscopic agglomerates, which consist of highly weathered oil enriched with hazardous compounds such as heavy PAHs, OxHCs, or EPFRs. Developing an understanding of the relationship between toxicity and changes in residue size is an excellent area for collaboration between the macroscopic and microscopic communities.

The overall knowledge of the in situ toxicity levels of both microscopic and macroscopic oil-sediment residues is currently limited. Additional in situ and mesocosm studies are recommended to better understand if and how toxic compounds trapped in SOAs and SOMs may partition into the surrounding medium to affect various species, and how OPAs that are formed from different types of oil and sediment may affect benthic habitats. Such studies can provide guidance for implementing remediation strategies to ensure that more good than harm is done to the afflicted environment. Furthermore, similar to liquid dispersants, any attempts to artificially disperse oil by using solid dispersants to form OPAs can transfer volatile petroleum chemicals into the water column before they have had the time to naturally weather through volatilization. Yin et al. (2015) laboratory studies has shown that volatilization can rapidly remove about 30% of the oil mass within the first 5 h. Volatilization rates can be considerably higher under field conditions due to higher morning temperatures and strong solar radiation exposure. Volatilization can prevent several toxic petroleum compounds from partitioning into the water column and impacting the flora and fauna. The relative advantages and disadvantages of interfering with the volatilization step through application of any form of dispersant to a fresh oil spill, including the use of solid dispersants to form OPAs, are currently unclear.

7. 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 minimize the damage that oil spills may cause to shoreline environments, which support diverse ecology as well as critical fishing and tourism economies, it is important that we facilitate a robust exchange of ideas between researchers who study different aspects of oil spill management strategies and their long-term impacts. The intent of this review is to encourage discussions and collaboration between researchers that seek to understand the formation, fate, and impacts of microscopic aggregates and/or macroscopic agglomerates. We believe that fostering this exchange will help develop more robust and inclusive decisions to manage remediation activities for future oil spills.

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