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Effects of weathering on the dispersion of crude oil through oil-mineral aggregation

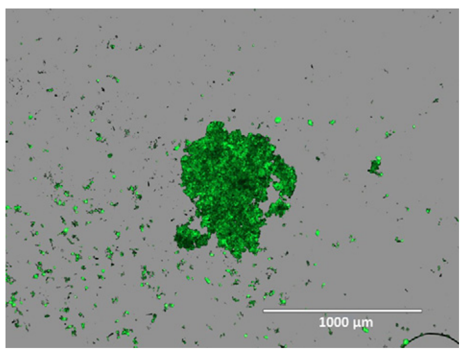
Sarah A. Gustitus, Gerald F. John, T. Prabhakar Clement *

Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL, USA

HIGHLIGHTS

- Different types of artificially weathered oils were used to study OMA formation.
- For all oil types, the amount of oil dispersed as OMA decreases with weathering.
- Reduction in OMA formation is controlled by physical rather than chemical effects.
- After 32 h of weathering, 35% of light and 1% of heavy crude were dispersed.

GRAPHICAL ABSTRACT



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ABSTRACT

Crude oil that is inadvertently spilled in the marine environment can interact with suspended sediment to form oil-mineral aggregates (OMA). Researchers have identified OMA formation as a natural method of oil dispersion, and have sought ways to enhance this process for oil spill remediation. Currently there is a lack of understanding of how the weathering of oil will affect the formation of OMA due to a lack of published data on this relationship. Based on literature, we identified two conflicting hypotheses: OMA formation 1) increases with weathering as a result of increased asphaltene and polar compound content; or 2) decreases with weathering as a result of increased viscosity. While it is indeed true that the viscosity and the relative amount of polar compounds will increase with weathering, their net effects on OMA formation is unclear. Controlled laboratory experiments were carried out to systematically test these two conflicting hypotheses. Experimental results using light, intermediate, and heavy crude oils, each at five weathering stages, show a decrease in OMA formation as oil weathers.

1. Introduction

When oil is inadvertently spilled in a marine environment, one of the major goals of remediation efforts is to disperse the unrecoverable oil into the water column to enhance various natural degradation processes. Dispersion increases the available surface area of the oil which enhances natural processes such as biodegradation and dissolution that play a significant role in degrading the oil (Prince et al., 2003; Prince et al., 1999). Oil can be naturally dispersed by turbulent currents caused by weather events, such as storms, as was observed following the *Exxon Valdez* oil spill (Wolfe et al., 1994). When weather conditions are insufficient to maintain sustained dispersion, chemical dispersants

* Corresponding author at: 212 Harbert Engineering Center, Auburn University, Auburn, AL 36849, USA.
E-mail address: clement@auburn.edu (T.P. Clement).

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are often used to promote oil dispersion. This approach was used in the aftermath of major oil spill events such as the *Torrey Canyon*, *Deepwater Horizon* and *IXTOC* oil spills (Jernelöv and Lindén, 1981; Kujawinski et al., 2011; Ramseur, 2010). However, there are several concerns about the potential negative toxic effects of chemical dispersants (Chapman et al., 2007; Linden, 1975; Ramachandran et al., 2004), hence it would be desirable to find environmentally friendly alternative dispersion methods to minimize their use until they are proven to be non-toxic.

When spilled oil enters the coastal environment, it can be dispersed naturally by interacting with suspended mineral fines to form small (typically <1 mm) aggregates in the water column (Bragg and Owens, 1995; Fitzpatrick et al., 2015; Lee et al., 1997). In the published literature, these microscopic aggregates are referred to as oil-mineral aggregates (OMA) (Lee et al., 1998). Trapping oil as OMA has been recognized as a method for enhancing oil dispersion, and has long been recognized to play a natural role in the remediation of oiled shorelines (Owens and Lee, 2003). Based on laboratory studies, researchers have postulated that OMA formation must have played a significant role in the natural cleansing of shorelines impacted by the *Exxon Valdez* spill (Bragg and Owens, 1995; Bragg and Yang, 1995). Field studies later confirmed natural OMA formation following the *Sea Empress* spill (Lee et al., 1997).

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

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

In addition to the "surf washing" method, some studies have suggested that oil spill remediation efforts can be enhanced by directly applying fine sediment to an oil slick to facilitate OMA formation (Bragg and Yang, 1995; Lee et al., 2011; Lee et al., 2012). More recent studies have explored various aspects of this idea in greater depth. Zhang et al. (2010) examined the efficiency of OMA formation with alternative materials such as fly ash and graphite that are not typically expected in a beach environment. Additionally, it has been found that modifying the surface properties of minerals such as bentonite or kaolinite can increase OMA formation (Chen et al., 2013; Wang et al., 2011; Zhang et al., 2010). Recently, a mesocosm study was carried out to determine the potential effectiveness of applying a slurry of sediment and water to oil contamination in a reflective beach environment; the study reported that over 21 days an average of a 40% reduction in saturated hydrocarbons was achieved (Silva et al., 2015). Lee et al. (2011) tested the sediment application method in a field study by releasing crude oil into the ice-infested St. Lawrence Estuary. Their team applied a slurry of calcite and seawater directly to the slick and then utilized the propellers of their vessel to create enough mixing energy to form OMA. They found that the oil was quickly dispersed by this treatment, with insignificant resurfacing of the oil. Additionally, mesocosm studies on samples from this field trial showed that over 56% of the spilled oil was degraded after two months, despite the low temperatures.

In order to determine the most effective way to enhance OMA formation, and to predict the natural extent of the aggregation, many studies have been carried out to better understand the fundamentals of the OMA formation process (Gong et al., 2014; Sun and Zheng, 2009). Through these studies, the impacts of several environmental variables including salinity, sediment concentration, temperature, mixing energy, sediment type and oil type have been explored (Gong et al., 2014). In addition to the effects of natural environmental factors, the effect of chemical dispersants on OMA formation has also been thoroughly studied (Cai et al., 2017; Guyomarch et al., 2002; Khelifa et al., 2008; Lee et al., 2012; Li et al., 2007; Wang et al., 2013). However, there is currently a gap in our understanding of how the degree of oil weathering will affect the OMA formation process over time (Sun and Zheng, 2009). Understanding this factor is crucial to extrapolating the results from idealized laboratory experiments, which are typically conducted using fresh oil or a single stage of weathered oil. Quantifying weathering effects on OMA formation will also help improve the capability of mathematical models used to predict the temporal variations in OMA formation, and can help develop guidelines for enhancing OMA formation for the treatment of oil spills. This knowledge can also improve risk assessments for environments where OMA form. For example, Niu et al. (2010) adapted their assessment of the risks of OMA to benthic organisms to account for variations in the chemical composition of weathered oil, but did not adjust the model to account for how the total amount of oil that could be transported to the benthic zone as OMA would change as the oil weathers.

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

Most OMA studies use only fresh oil, or a single weathered stage of an oil, and as a result there are some disagreements in the published literature about whether OMA formation increases or decreases as a result of weathering. Based on literature, we have identified two conflicting research hypotheses. We first hypothesize that increased relative quantities of polar and charged hydrocarbons, such as asphaltenes, found in weathered oil will cause an increase in dispersion through OMA formation by increasing the attractive forces between the oil and the negatively charged mineral surface (Bragg and Yang, 1995; Sørensen et al., 2014; Stoffyn-Egli and Lee, 2002). Bragg and Yang (1995) found that