Photochemical transformations of oil at sea: implications for response operations

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Abstract:

In this presentation and article, we synthesize findings from a workshop about our understanding of the interplay between crude oil photochemical oxidation and oil spill response, emphasizing how this understanding has evolved since the 2010 DWH spill. Our discussion is guided by one overarching questions: what role does photochemical oxidation play towards informing effective oil spill response operations? We show that prior to the DWH spill, our understanding of the relative importance of oil weathering processes, specifically photochemical weathering, was incomplete. We further explore how accounting for photochemical changes to oil's properties (physical and chemical) could improve the effectiveness of oil spill response operations, specifically chemical dispersant applications. Lastly, we identify priority knowledge gaps related to this guiding research question.

Introduction:

When oil is released into the environment it undergoes a series of weathering processes, including dissolution, evaporation, photochemical oxidation, emulsification, biological degradation, and sedimentation. Figure 1 depicts these processes for a spill at depth in the water column, similar to the 2010 *Deepwater Horizon* (DWH) spill. Some of these processes (dissolution, evaporation, and sedimentation) move the oil to different locations and can change the physical properties of the oil, but the chemical properties of the hydrocarbons that make up the oil remain unaltered. For example, low molecular weight alkanes, like octane, are largely insoluble in water but very volatile, so they rapidly evaporate to the atmosphere. Octane is lost from the liquid oil, but not chemically transformed in the process. In contrast, higher molecular weight alkanes, like octadecane, are also largely insoluble in water and much less volatile. Although no chemical transformation occurs, octadecane will contribute to the mass of insoluble, non-volatile oil floating on the sea surface (i.e., surface oil). However, loss of compounds due to, for example evaporative weathering, do change the physical properties of the oil making the floating fluid more viscous and denser.

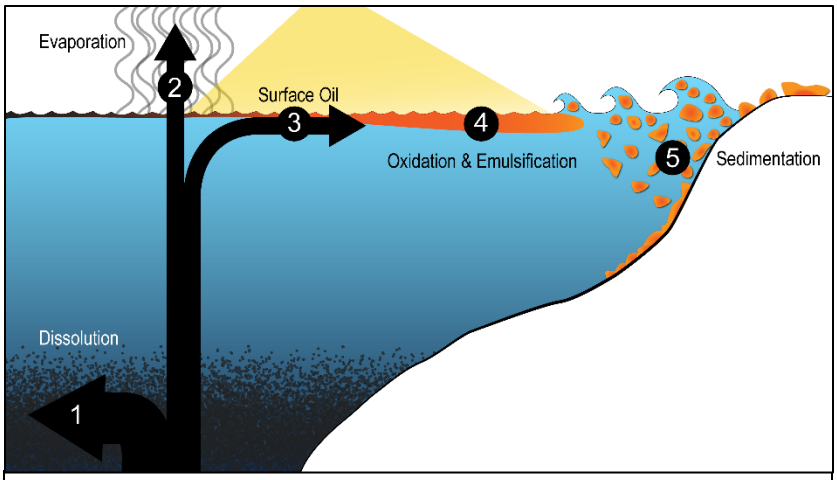

Figure 1. Weathering of oil in marine waters. Here, the spill occurs at depth in the water column, although these general processes also occur for surface spills.

Emulsification is a weathering process where water is mixed with and retained by the floating oil. No alterations to the chemical properties of oil occur due to emulsification, but physical properties are substantially altered, including density and viscosity. Near the coast, some of this emulsified oil can get mixed with solids in near shore intertidal areas and be deposit on the sea floor or on beaches and marshes, in a process collectively referred to as sedimentation. Importantly, no chemical transformations of the oil occur during sedimentation, it is merely a translocation process.

Photochemical and biological oxidation are transformative processes where the oil is oxidized by sunlight or microbes into CO_2 or new oxygenated compounds. If the hydrocarbons are completely oxidized to CO_2 (a gas), oil components are lost from the floating oil. However, if the hydrocarbons are partially oxidized into new compounds, the parent compounds may not be lost from the oil, but rather transformed into new components that increase the complexity of oil's chemical composition. These new chemical components of the oil can have vastly different physical and chemical properties than the parent hydrocarbons, and thus change the physical and chemical properties of the floating oil. Some of these newly oxidized oil components are water soluble and enter the waters surrounding the spilled oil, while other oxidized components are retained in the floating oil. A fraction of these oil soluble photo-products will associate with the oil water interface and impact emulsion formation potential. Our understanding of the relative importance of these photo oxidizing weathering processes, and the impact of these processes on oil spill response operations and damage assessments, is currently being re-evaluated and updated with information learned following the DWH spill.

The goal of this presentation and article is to synthesize how our understanding of the interplay between crude oil photochemical oxidation and oil spill response has changed since the 2010 DWH spill. Our discussion is guided by one overarching questions: what role does photochemical oxidation play towards informing effective oil spill response operations? We show that prior to the DWH spill, our understanding of the relative importance of oil weathering processes, specifically the photochemical oxidation, was incomplete. We further explore how accounting for photochemical changes to oil's properties (physical and chemical) could improve the effectiveness of oil spill response operations, specifically the formation of stable water-in-oil emulsions and chemical dispersant applications. Lastly, we identify priority knowledge gaps related to this guiding research question.

What role does photochemical oxidation play in oil spill response?

What we knew prior to the DWH spill

It is well established that as oil weathers at the sea surface, the effectiveness of tools used to respond to oil spills decreases. The term "window-of-opportunity" is used to define the time after a spill where an effective response can be achieved. Although the "window-of-opportunity" varies for different tools, oils, and spill locations, the general consensus prior to DWH was that evaporation and emulsification were the two most important weathering process impacting oil spill response decisions. The rationalization behind this consensus was that these two processing impact the physical properties of oil, specifically viscosity and density. For example, the 2005 National Academies report on dispersant use for marine oil spills explicitly states that "the two most important weathering factors include evaporation and the formation of stable water-in-oil emulsions, because they both affect the spilled oil's *in situ* viscosity on the water surface."

Moreover, “viscosity was found to be the most important physical property in determining dispersibility.” The Exxon Mobil oil spill response manual states that “viscosity changes affect the selection of response options,” and “emulsification and mousse formation increase the density and viscosity, which may affect the selection of clean up options.”

Numerous conceptual diagrams (ExxonMobil 2014, Oil Spill Response Limited 2013) depicting the relative importance of different weathering processes characterized photochemical oxidation of floating surface oil as a minor, secondary process relative to evaporation, emulsification, and biodegradation (Figure 2). In these conceptual models, the importance of the process is represented by the size of the bar and time since the spill is shown on the x-axis. Evaporation is often the largest bar on the diagram, starts immediately after the spill, and lasts up to a year. Emulsification is a much smaller bar than evaporation, starts hours after the spill, and lasts up to a year. The biodegradation bar is typically the same size as emulsification,

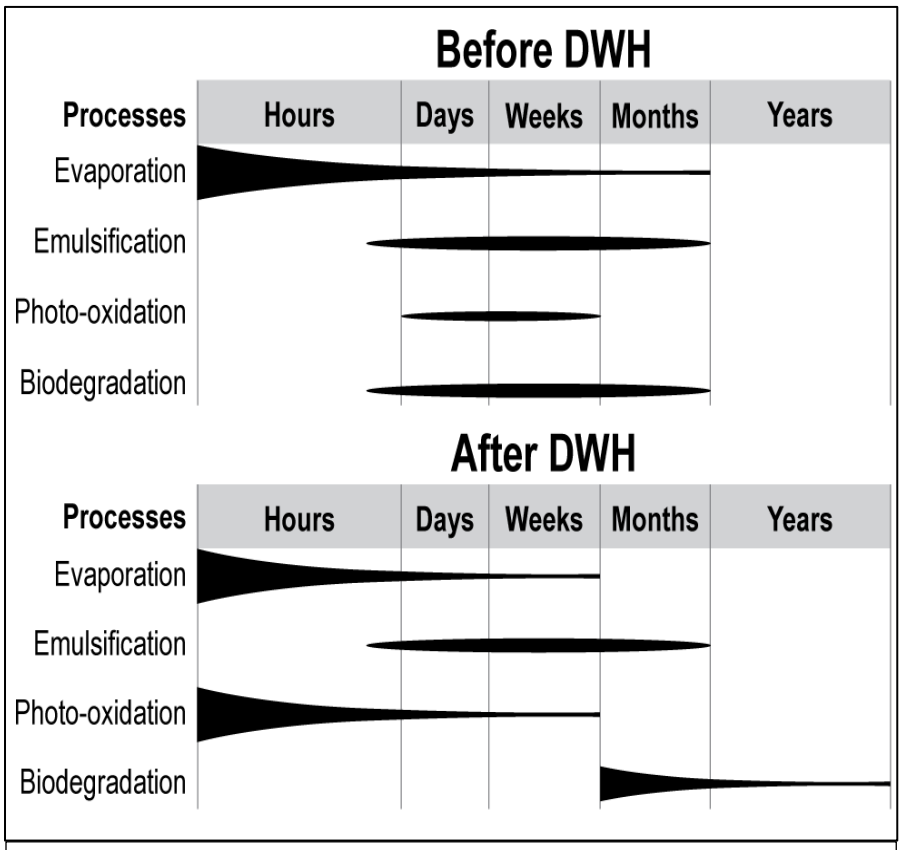

Figure 2. Conceptual models depicting the relative importance of different weathering processes of floating surface oil at sea.

starts several hours after the spill, and lasts up to a year. Photochemical oxidation is consistently the smallest bar on the diagrams, starts days after the spill, and lasts up to a week. Collectively, the consensus perspective prior to the DWH spill was that sunlight-driven processes have little impact on the fate, transport, or response to oil spilled into the ocean because it is a slow, secondary weathering process impacting a minor fraction of spilled oil.

Accordingly, response operations do not consider the extent of photochemical weathering when determining how best to optimize response effectiveness. In fact, the Exxon Mobil oil spill response manual explicitly states that the effects of photochemical oxidation are "negligible relative to other weathering mechanisms." Moreover, an international oil spill response cooperative that provides consulting services to all major oil companies in response to spills, Oil Spill Response Limited from South Hampton UK, describes oil oxidation in their response guidance documents as follows: "oil reacts with oxygen to form new by-products, including soluble products or persistent tars. The process is promoted by sunlight (photo-oxidation). The process occurs at the surface of the oil and even in the strong sunlight, is very slow." In the United States, the National Oceanic Atmospheric Administration's Guide for Spill Response Planning in Marine Environments (2019), oil oxidation isn't even mentioned, whereas evaporation and emulsification are discussed frequently. Collectively, this perspective suggests that the response plan or the "window-of-opportunity" to respond effectively to an oil spill is not influenced by the extent of photochemical oxidation.

This perspective overlooks multiple instances in the literature where photochemical oxidation was reported to have substantial impacts on the physical properties of oil, including viscosity and

mousse formation. Most notably, Thingstand and Pengerud 1983 reported that visible light exposure (i.e., > 400 nm) and physical mixing play essential roles in the formation of water-in-oil emulsions, also known as "mousse" (Figure 3). In their study, laboratory incubations with Statfjord crude oil (a light sweet crude from the North Sea) were conducted under varying environmental conditions (light, shaking speed, and temperature). The amount of water incorporated into the oil during the incubations was quantified, as was the establishment of stable water-in-oil emulsions. The treatments with high light and shaking speed, those optimized for photo-oxidation, retained the most water and most quickly formed stable water-in-oil emulsions. For example, the amount of water incorporated into a Statfjord crude oil after six days of visible light exposure and shaking at 15°C was nearly 7-fold higher than the same oil shaking in the dark. Decreasing irradiance and shaking speed retarded emulsification but decreasing temperature did not. Moreover, in the same experiment, the addition of beta-carotene to the light-exposed treatment yielded the same amount of water uptake as the dark control. Beta-carotene is a well-known quencher of singlet oxygen, a reactive intermediate produced by sunlight

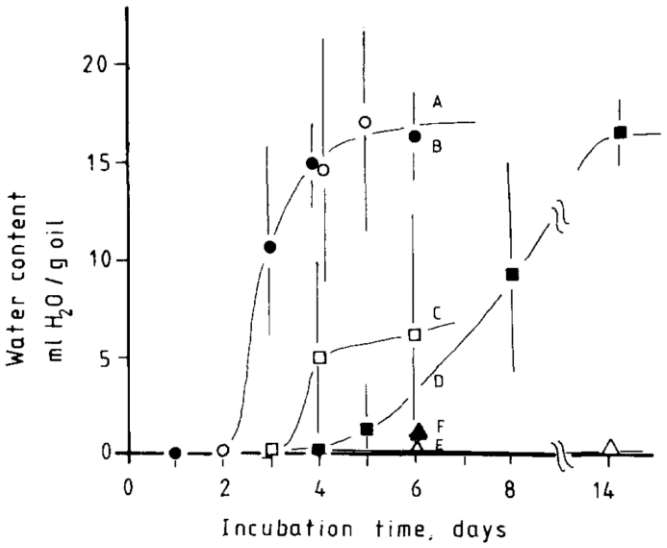

Figure 3. The formation of water-in-oil emulsions as defined by water content in Statfjord crude oil exposed to varying laboratory conditions (visible light, shaking speed, and temperature). **A**- open circle: high light, shaking, and temperature. **B** - closed circle: high light and shaking, but low temperature. **C** - open square: high light, low shaking, and high temperature. **D** - closed square: low light, high shaking and temperature. **E** - open triangle: no light, high shaking and temperature. **F** - closed triangle: no light, high shaking, low temperature. Figure modified from Thingstad and Pengerud 1983.

and hypothesized to play a major role in initiating oil photochemical oxidation (Larson and Hunt 1979, Nicodeem 2003). The authors even hypothesized a mechanism for the formation of water-in-oil emulsions. The photochemical formation of polar groups in large, hydrophobic molecules act as oil-soluble, surface-active argents that cause water droplets to be retained during physical mixing. Prior to the DWH spill, this hypothesized mechanism had not been explicitly tested, in large part because some of the analytical technologies required to test this hypothesis were not available.

This primary research was included in a 1985 review article written Payne and Phillips, where the authors explicitly state that "changes in viscosity, spreading or contraction rates, and water-in-oil emulsification tendencies also may occur as a function of oil photooxidation." They go on to state that these light-driven "changes can occur at rates comparable to evaporation," a weathering process that is routinely considered to affect the selection of response tool (NAS 2005, ExxonMobil (2014), Oil Spill Response Limited (2013)). Nevertheless, prior to DWH, photochemical oxidation was considered a weathering process that promoted emulsifications, but with a negligible impact on response operations.

What we learned from the DWH spill

Dozens of field and laboratory studies (e.g., Aeppli et al., 2012; Hall et al., 2013; Lewan et al., 2014; Ruddy et al., 2014; Cao and Tarr, 2017; Seeley et al., 2018; Ward et al., 2018b; Ward et al., 2019) using a myriad of approaches (biomarker analysis, mesocosm experiments, and photochemical rate modelling) and analytical tools (GC-FID, GC-MS, TLC-FID, FTIR, elemental analysis, FT-ICR MS, NMR, stable isotope analysis, and pyrolysis GC-MS) all point towards the

same conclusion: *photochemical oxidation was the governing process of surface oil oxidation in the aftermath of the DWH spill*. Further, results from field residues and laboratory photo-oxidation experiments supports the conclusion that upward of 50% of the floating surface oil was oxidized by sunlight in less than one-week (Ward et al., 2018b). These consensus points and laboratory studies challenge the community perception that photochemical oxidation is a minor, secondary weathering process that operates on timescales of weeks to months. Accordingly, conceptual models depicting the role of photochemical weathering in the fate and transport of spill oil have been changed to accurately reflect the role of sunlight (National Research Council, 2019; Figure 2).

One key, response-relevant finding from researching the DWH spill was that sunlight exposure substantially alters the physical properties of crude oil at the sea surface. By systematically testing the change in density, viscosity, and adhesion as a function of evaporation and photochemical oxidation, the relative importance of these weathering processes could be evaluated. Simulated sunlight exposure of crude oil to the equivalent of < 3 days of natural sunlight in the GoM resulted in a two-fold greater increase in density, a three-fold greater increase in dynamic viscosity, and a two-fold greater increase in adhesion compared to the same oil that was evaporated to 30% mass loss (Ward et al., 2018a). These results corroborate previous reports (Payne and Phillips 1985) that photochemical oxidation can impart major changes to the physical properties of crude oil, comparable in magnitude to evaporation.

Another key, response-relevant finding from researching the DWH spill was that sunlight is a key process in the formation of water-in-oil emulsions. Using a novel method developed to isolate

surface active molecules (Clingenpeel et al., 2015) and FT-ICR MS, Zito et al., 2020 elegantly demonstrated that photochemical oxidation yields compounds that partition to the oil water interface and effectively behave as emulsifying agents. This is a critical finding because it corroborates the hypothesis put forth by Thingstad and Perengrud 1983, a hypothesis that was not testable at the time due to analytical limitations (i.e., both the isolation approach and FT-ICR MS). This finding is also critical because it validates a "new view" that, for some oils, emulsification weathering is a secondary process promoted by photochemical oxidation, a primary weathering process (Figure 2). Note, some oils easily form emulsions, while others need weathering transformations, such as photo-oxidations, that produces stabilizing chemicals in the oils required to form emulsions.

Lastly, through a combination of mesocosm experiments, kinetic modeling, and geospatial analysis, it was determined that photochemical oxidation of DWH surface oil had the potential to greatly hinder the performance of chemical dispersants (Ward et al., 2018a). For example, laboratory simulated sunlight exposure of crude oil to the equivalent of <3 days of natural sunlight in the GoM resulted in a ~30% reduction in dispersant effectiveness. Importantly, the magnitude of this decrease in dispersant effectiveness due to photochemical oxidation exceeded that of evaporation (30% mass loss) by four-fold. This finding challenged the prevailing assumption that, at least for oils with chemical compositions similar to those produced in the northern Gulf of Mexico, the effects of photochemical oxidation are negligible relative to other weathering mechanisms (ExxonMobil 2014). When accounting for photochemical oxidation, modelling efforts suggest that a considerable fraction of aerial applications targeting DWH surface oil may have had lowered dispersant effectiveness (Figure 4).

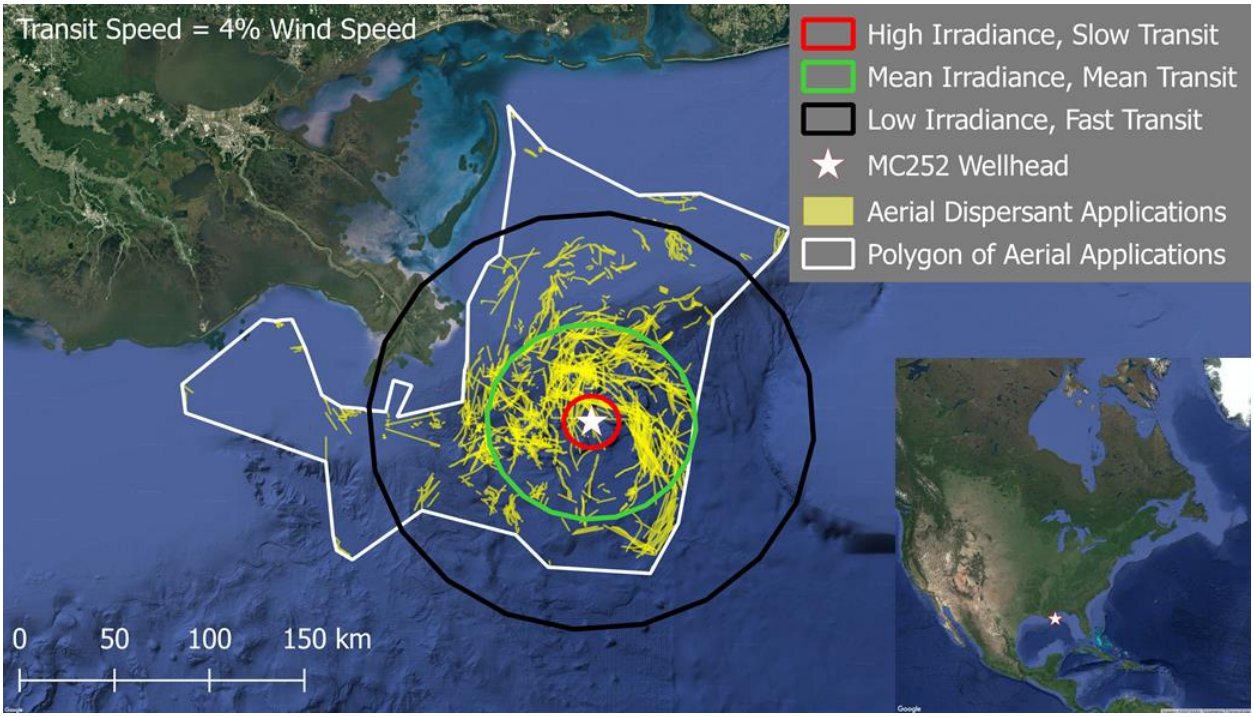

Figure 4. The location of the Macondo well in the GoM is indicated by the white star. The location of the 412 flight paths for aerial dispersant applications are presented in yellow and are outlined by the polygon in white. Each concentric circle represents the distance DWH surface oil travelled before photo-oxidation decreased dispersant effectiveness to < 45%, assuming three irradiance/speed categories: high irradiance and slow transit speed (red inner circle), mean irradiance and transit speed (green intermediate circle), and low irradiance and fast transit speed (black outer circle). Under mean conditions, a substantial fraction of aerial applications targeted oil that had low effectiveness. Modified from Ward et al., 2018a.

The exact mechanism behind the apparent decrease in dispersant effectiveness is unknown. One explanation could be the low solubility of photochemically oxidized oil in the carrier solvent of dispersants (food-grade kerosene). This incompatibility would limit interaction between the surfactant molecules in the dispersant mixture and the oil, perhaps limiting the amount of oil that can be chemically dispersed. Another plausible mechanism could be the photochemical production of surface-active molecules that act as emulsifying agents and retained water which in turn limited dispersant-oil interactions (Thingstad and Peringrud 1983, Zito et al., 2020). Emulsified oils are known to be difficult to disperse. Independent of the mechanism, laboratory studies to date support

the conclusion that sunlight plays a critical role in the alteration of crude oil properties (both physical and chemical), and this may impact the performance of chemical dispersants applied in response to oil spills at sea. This new perspective is now incorporated into updated guidance documents for the weathering of oil at sea and the use of dispersants in response to oil spills (NAS 2019).

High Priority Questions for Future Research

As with all lines of research, more questions are often raised than answered. Below we have provided a list of five research questions that we view as high priorities to advance our understanding of the impact of photochemical weathering on oil spill response operations:

1) How does the rate and extent of photochemical oxidation vary for different types of oils (e.g., light to heavy, sweet to sour) under different environmental conditions (e.g., light, temperature, salinity, pH)?
2) Is the decrease in dispersant effectiveness caused by photochemical oxidation similar for different oil and dispersant types?
3) Are chemical agents other than dispersants impacted by photochemical weathering, such as surface washing agents, herders, emulsion breakers?
4) How does the stability and behavior of water-in-oil emulsions depend on the extent of photochemical oxidation?
5) What steps must be taken to accurately translate results from laboratory experiments or tank tests into information that can be used by the oil spill response community?

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