

## **Review of the Science behind Oil Spill Fate Models: Are Updates Needed?**

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### **Abstract (687874)**

Oil spill models play an important role in the oil spill response decision making and contingency planning processes. The current generation of spill models mostly use Lagrangian based particle tracking random walk methods for oil transport processes combined with individual algorithms for oil fate processes (Spaulding, 2017). The fate of near surface oil movement is modeled using algorithms describing oil spreading, evaporation, emulsification, entrainment, dissolution, and biodegradation. These fate processes are applied to oil in the Lagrangian particle tracking elements to alter the physical and chemical properties of the oil, and subsequently the oil behavior.

In this paper, we review the major algorithms used in oil spill models and identify the science and physics underpinning them. For each, we evaluated how far the science has advanced since the algorithms were developed to identify those that could be upgraded based on current understanding. We also identified algorithms where future research is needed because the physical and chemical behaviors are not fully understood. These areas include the spreading behavior of surface slicks, surface-slick emulsification, and the physical transport of small oil droplets near the air-water interface.

## **Introduction**

The fate and behavior of spilled oil on marine and freshwater surfaces can be affected by many processes that change oil properties with time and distance from the source. Early efforts to model fate processes relied on empirical correlations calibrated by experimental data. These correlations form the basis of most oil spill fate models in use today. Reviews of the state of the art in oil spill models have been conducted over the years. Stolzenbach et al. (1977) conducted a review of basic techniques for predicting the behavior of surface oil slicks. Huang (1983) conducted an overview of over thirty oil spill models capable of simulating various physical, chemical, and biological processes that affect the fate of spilled oil. Since then, the modeling techniques and knowledge of many of the oil spill fate processes have advanced. Recently, Spaulding (2017) conducted a brief review of the current state of development of oil spill models and provided a guidance for future development. We complement these reviews in the current work and attempt to provide a prioritization of the improvement needs for the individual fate algorithms.

The objective of the present paper is to review the major algorithms used to predict the fate of oil spilled on a water surface. The processes include oil spreading, evaporation, emulsification, dispersion, dissolution, and biodegradation. We evaluate the development of each algorithm and identify those that could be upgraded based on advances in current understanding of oil behavior.

## **Oil Spreading**

Spreading is the major processes affecting the fate of spilled oil. The spreading rate determines the oil slick thickness and water surface area covered by oil, which also influences the rates of other processes, such as evaporation, emulsification, dispersion, and subsequently

affects oil transport, dissolution, and biodegradation (Berridge et al., 1968; Stolzenbach et al., 1977). Accurate estimates of the geographic coverage and volume of oil is also important for clean-up strategies, and for economic, environmental and legal purposes (Lehr et al., 1984).

Based on an understanding of the forces that cause or retard spreading, Fay (1971) and Hoult (1972) developed relationships describing spreading of oil on a calm sea. They divided spreading into three consecutive flow regimes (Fay, 1971):

1) Gravity-inertia

$$\frac{dA}{dt} = k_1^2 \pi (\Delta g V)^{1/2} \quad (1)$$

2) Gravity-viscous

$$\frac{dA}{dt} = \frac{1}{2A} \left[ k_2^2 \pi \left( \frac{\Delta g V^2}{v_w^{1/2}} \right)^{1/3} \right]^2 \quad (2)$$

3) Viscous-surface tension

$$\frac{dA}{dt} = \frac{3A^{1/3}}{2} \sqrt[3]{k_3^4 \pi^2 \frac{\sigma^2}{\rho_w^2 v_w}} \quad (3)$$

where A is the surface area covered by oil;  $k_1$ ,  $k_2$ , and  $k_3$  are the spreading law coefficients for the three flow regimes, respectively; V is the volume of oil;  $\Delta g = \frac{\rho_w - \rho_o}{\rho_w} g$ ,  $\rho_w$ ,  $\rho_o$  are density of water and oil, respectively, g is acceleration of gravity;  $v_w$  is the kinematic viscosity of water;  $\sigma$  is interfacial tension between oil and water. .

The first stage of the Fay-Hoult spreading theory, gravity-inertia, lasts a very short time (i.e. minutes), while the third (also the last) stage could occur over days allowing significant weathering to occur at the same time as spreading. This weathering could significantly alter the physical/chemical properties of the oil, and consequently the theoretical behavior of the slick as posited by Fay. The second stage of spreading, the gravity-viscous regime, dominates in between the first and third stages and the time frame depends on the spill size (e.g. last a few hours for a

~1000 bbl spill, Jeffery, 1973). This spreading regimes has been widely adopted in modern oil spill models (e.g. Chebbi, 2001; French-McCay et al., 2017; Lehr et al., 1984; Maderich et al., 2012). Since Fay and Hoult, efforts have been made to improve the spreading law coefficients.

Previous studies showed that Fay's theory resulted in good agreement with laboratory experimental results for one dimensional cases (Fannelop and Waldman, 1972; Fay, 1971; Hoult, 1972), but greatly underestimated the spreading rate in the field (Elliott et al., 1986; Lehr et al., 1984; Murray, 1972). On-site observations during large scale field experiments and spill events reported that oil slicks tend to spread/elongate in the direction of the wind, a much higher rate than predicted by Fay's theory (e.g. Cormack and Nichols, 1983; Jeffery, 1973; Lehr et al., 1984). To account for slick elongation in the wind direction, Lehr et al. (1984) developed a modified Fay-type spreading formula based on Fay's second spreading regime (gravity-viscous), where they constrained the slick to have an elliptical shape and added an additional wind forcing term along the major dimension of the ellipse. Elliott et al. (1986) considered entrainment of oil droplets through vertical shear diffusion effects in the near surface horizontal currents followed by the subsequent resurfacing of oil droplets. Due to the different buoyancy of the entrained droplets, slick will form a comet shape where thick oil formed by the resurfacing of large droplets appear at the downwind end of the slick with sheen trailing behind because of the slow ascending of smaller droplets.

Oil slicks are never homogeneous. It has been observed in the field that sheen forms rapidly after the oil is released on the water surface, surrounding a thicker oil pool (Jeffery, 1973). Figure 1 shows the surface release of two crude oils on seawater in a 1 m<sup>2</sup> square pan. The low viscosity Alaska North Slope (ANS) crude oil spread quickly forming a thick oil patch surrounded by sheen (Figure 1a), while the high viscosity fuel oil spread slowly form a thick

center pool surrounded by sheen (Figure 1b). For both cases, sheen is formed almost instantaneously in the leading edge of the oil pool after the release, and spreads faster than the thick, center oil pool. Such sheening behavior is not captured in the Fay-Hoult's theory. Mackay et al. (1980) attempted to characterize the spreading of thick and thin patches by arbitrarily assigning a thin slick of constant thickness (1 micron) drawing oil from the thick patches as it spreads. However, their approach is empirical and lacks a rational physical basis. To the best of our knowledge, the understanding of sheen formation is limited, very few experiments have been conducted, and numerical prediction algorithms are nonexistent. Phillips and Groseva (1975) and Peterson and Berg (1986) have shown that the chemical composition of the sheen may also vary with location and time. As the sheen expands to cover a larger surface area (~80% of the total spill area) (Jeffery, 1973), the fate of oil sheen lost to evaporation and entrainment (oil dispersed into the water column) could be significant as the sheen will evaporate and naturally disperse faster than thicker oil patches.

Oil viscosity is another major factor that influences spreading behavior as shown in Figure 1. However, oil viscosity is not accounted for in the Fay spreading schemes (see Eqs. 1-3). Using Fay-Hoult's second stage of spreading, the gravity-viscous regime, predictions of the spreading area after oil release for the two oils are shown in Figure 2, as shown along with the experimental observations. The gravity-viscous phase significantly underestimates the spreading of the low viscosity ANS oil (Figure 2a); but, closely reproduces the surface area of the high viscosity fuel oil (Figure 2b). The predictions using the third phase, the viscous-surface tension, at the time period that the image was taken are also plotted in Figure 2. The surface tension spreading overestimates the sheen area. Results from Figure 2 suggest that the gravity-viscous regime may only accurately apply to very high viscosity oils to predict the size of the oil pool.

In summary, the spreading algorithms that are used in oil spill models basically follows Fay-Hoult's theory, and efforts have been made to improve the field predictions in the open ocean over the years. However, the current modeling approaches still have limitations even on calm and stationary water conditions, which could be further improved in the future:

- a) Oil sheening has been observed in the lab experiments and field studies, however, the physical/chemical behavior of sheening cannot be predicted via the current modeling techniques. One may argue that the amount of oil forming the sheen only occupy small mass of the total spilled oil; but oil sheening is a continuous process almost throughout the lifetime of spilled oil, which is a major contributor to the disappearance of oil naturally in the open sea.
- b) Future development of spreading algorithms need to account for the effects of oil viscosity, which apparently has major effects on the spreading rate.

### **Oil Evaporation**

Oil evaporation from surface slicks can contribute significantly to oil mass loss soon after oil has reached the surface. Typical crude oils may lose ~25-40% of their volume to evaporation in the first a few days (Fingas, 2015; Lehr et al., 2002). Modeling of oil evaporation basically follows Raoult's law. The most commonly adopted mass transfer rate due to evaporation can be expressed as (Fingas, 1999, 2015; Galagan et al., 2018; Mackay and Matsugu, 1973; Tkalin, 1986):

$$\frac{dm}{dt} \propto K_e \frac{PA}{RT} M \quad (4)$$

where  $m$  is the oil mass lost to evaporation;  $K_e$  is the mass transfer coefficient, the subscript  $e$  represent evaporation;  $P$  is vapor pressure;  $A$  is slick surface area;  $R$  is universal gas constant;  $T$  is temperature; and  $M$  is relative molecular weight.

The mass transfer coefficient represents the hydrodynamics at the liquid-air interface (Brutsaert, 2013), and many of the evaporation studies follow the mathematical expression for water evaporation developed by Sutton (1934), where the mass transfer coefficient is a function of wind speed, size of the liquid body, and Schmidt number, expressed as:

$$K_e \propto U^{7/9} d^{-1/9} Sc^{-2/3} \quad (5)$$

where U is wind speed; d is slick diameter; and Sc is Schmidt number.

Mackay and Matsugu (1973) calibrated Eq. 5 to hydrocarbons using data on the evaporation of cumene. They then compared the calibrated predictions of gasoline evaporation to experimental data and found fair agreement. Drivas (1982) also compared Mackay and Matsugu's equation with literature data and found that the predictions were close to the experimental data. Mackay and Matsugu's equation is currently adopted in the SIMAP model (Galagan et al., 2018). Stiver and Mackay (1984) built on Mackay and Matsugu's work and made significant additions to the evaporation schemes, including terms for the volume fraction evaporated, and a ratio called evaporative exposure which can be viewed as the ratio of exposed vapor volume to the initial liquid volume (Fingas, 2015). Stiver and Mackay's work have been frequently used in spill modeling over the years (e.g. Fingas, 2015; Hamoda et al., 1989; Lehr et al., 2002; Tkalin, 1986). Bobra (1992) compared Stiver and Mackay's model to extensive experimental data of oil evaporation, and reported that the model performed well for the first eight hours, but overestimated long term evaporation in most cases.

Crude oil is a mixture of hundreds (if not thousands) of compounds and this mixture varies from source to source and over time as natural processes alter the oil composition (Fingas, 2015). Each compound has its own evaporation rate, and information on the evaporation rates of different compounds in crude is not available and might not be practical to model in any event.

Therefore, in many spill models (Galagan et al., 2018; Jones, 1997; Lehr et al., 2002 , etc.), pseudo-components are used to simplify prediction of weathering processes. Jones (1997) developed a simplified pseudo-component oil evaporation model. He grouped the representative evaporation compounds into a relatively small number (6) of discrete, non-interacting components. Each pseudo-component evaporates according to its vapor pressure, diffusivity, and molecular weight. Galagan et al. (2018) extended from 7 to 19 volatile pseudo-components derived by weighted averages of properties of the group of chemicals included in the component. The evaporation rate (Eq. 5) is then computed based on the properties of individual pseudo-components, and the total evaporation rate is the sum of the individual rates.

Recent studies by Fingas (2011); Fingas (2015) challenged the traditional oil evaporation models as discussed above. He argued that the diffusion of oil compounds within the oil slick is the main drive for the oil evaporation rather than the air boundary layer process. He conducted evaporation experiments in wind tunnels and found that the changes of evaporation rates with increasing wind speed are relatively small. Based on these results, he proposed empirical equations where the evaporation rate of oil is only dependent on the temperature and time. Spaulding (2017) reviewed Fingas's work on evaporation, pointed out that Fingas' theory may not represent conditions at sea, and concluded his empirical formulations on oil evaporation are not practical in oil spill modeling exercises as it treats the oil as a whole.

In essence, the current evaporation modeling schemes in oil spill models are based on the mass transfer in the boundary layer between oil film and atmosphere. The mass transfer coefficients were developed from the ones originally developed for water evaporation, with modifications to fit the evaporate rate for oil compounds. The predictions are seemingly able to achieve certain degrees of accuracy by comparing with lab experimental data in literatures. New



theory on oil evaporation have been proposed in recent years. More experimental data are needed to calibrate and validate the current algorithms, and to test the new theory for practical use in oil spill models.

### **Oil Emulsification**

Oil emulsification is the process where small water droplets are trapped in an oil-continuous phase to form a water-in-oil emulsion. Oil emulsification may dramatically change the physical properties of spilled oil. For example, for stable emulsions containing >60% water, the oil viscosity can increase 500 times, and the volume of the spilled oil by 2-5 times (Fingas, 2015). The increase in viscosity and total volume due to emulsification challenges all response options (NRC, 2003).

The current theory is that the polar asphaltenes and resins in crude and fuel oils are believed to be the major promoters for the stability of water-in-oil emulsions (Bobra, 1992). Fingas and Fieldhouse (2012) studied the formation of water-in-oil mixtures on over 300 crude oils and petroleum products and found that oil emulsification is a result of the physical stabilization by the initial oil viscosity and is sustained through chemical stabilization by asphaltenes and resins. They grouped the water-in-oil mixtures into four classes: stable (>~76% of water content, normally refer to as “mousse”), meso-stable (~66% of water content initially, then drop to ~30% after a week, reddish-brown viscous liquid), entrained (~46% of water on the first day, then drop to <28%, black viscous liquid), and unstable (very small amount of water, normally light fuels like diesel, or very high viscous oil products). In their comprehensive review on emulsions, Goodarzi and Zendeboudi (2019) elucidated that droplet size is another major parameter that characterize the emulsion stability, stating that only micro-emulsions with a droplet size in the nanometer scale form stable emulsions thermodynamically. Boxall et al.

(2012) proposed a formula to obtain the maximum droplet size in water-in-oil emulsion using Weber number and Reynolds number in the inertial and viscous subranges under turbulent flow.

The emulsification scheme developed by MacKay and Zagorski (1982) has been used in many spill models. It describes the emulsification rate as a function of wind speed, expressed as follows:

$$\frac{dF_w}{dt} = CU_w^2 \left(1 - \frac{F_w}{F_{wmax}}\right) \quad (6)$$

where  $F_w$  is fraction of water in oil;  $C$  is an empirical constant;  $U_w$  is wind speed;  $F_{wmax}$  is the maximum fraction of water in fully emulsified oil.. The maximum water content is a function of viscosity. Mackay's equation does not account for the demulsification of meso-stable and unstable emulsions. Xie et al. (2007) modified Mackay's formulation and included demulsification using an exponential decay curve for meso-stable and unstable emulsions.

Departing from Mackay's formulations, Fingas (2015) proposed a factor called the stability index which was estimated empirically based on their extensive database of emulsions. If-then statements were used to estimate the corresponding water content, oil density, viscosity, and asphaltene / resin contents. They claimed that their model was superior to Mackay's model in predicting oil properties (Fingas, 2015). However, their model was purely empirical, and was not developed based on physical and chemical mechanisms. Based on Fingas modeling theory, Galagan et al. (2018) later on added the stability class in their model to estimate oil properties.

Lehr (2017) combined the traditional modeling approach with Fingas' cluster modeling approach and adopted a set of rules governing emulsion stability based on literature data. The literature data was widely scattered, which led to a poor fit between their predictions and the data (Barker et al., 2019).

Although knowledge of water-in-oil emulsification has advanced significantly over the last several decades, most of this understanding is based on empirical findings that have led to empirical relationships. Model development to capture the physical and chemical mechanism of oil emulsification is still in its early development. A more theoretical understanding of the specific components of crude / fuel oils, the influence of photo-oxidation, and behavior of emulsions in an open system would lead to development of more accurate models. Further, we are concerned that the protocols used to create water-in-oil emulsions in the lab may not satisfactorily represent conditions in the field. For example, we know of no lab-based testing that included photo-oxidation. In addition, lab protocols don't allow emulsions to spread on open water and don't allow dissolution of oil components in an open system. In order to advance to a theoretical understanding of emulsification formation and stability, more representative test protocols are needed.

Based on our analysis we propose the following development needs for emulsification algorithms:

- a) Identify key factors that lead to the emulsion formation and affect the stability based on current understanding of oil-in-water emulsion during spills in open water. These factors may include photo-oxidation, mixing energy, oil properties, etc.
- b) Develop new experimental protocols that could represent conditions in the field as close as possible, focusing on the variations of key factors. Conduct experiments based on the new protocols to enhance the theoretical understanding of oil emulsion.
- c) Develop reliable algorithms/correlations that appropriately relate emulsion formation mechanisms and emulsion stability to the key factors based on the new experimental data.

## **Oil Dispersion**

Oil dispersion refers to the process of surface oil breaking into small droplets due to wave actions and entraining into the water column. The result is a continuously diluting weathered oil (e.g. the opposite of the water-in-oil emulsification discussed above). The most widely used modeling scheme for describing oil droplet size distribution due to breaking wave events is the empirical formula developed by Delvigne and Sweeney (1988), expressed as:

$$N(d) \propto d^{-b} \quad (7)$$

where  $N$  is the number of droplets with a diameter  $d$ ,  $b$  is a constant ( $b=2.3$ ). Eq. 7 was further transformed to describe the mass flux of oil dispersed from the sea surface to the water column as (Delvigne and Sweeney, 1988; Johansen et al., 2015):

$$q_i = C E_w^{0.57} F_{bw} d_i^{0.7} \quad (8)$$

where  $q_i$  is entrainment rate per unite surface area of oil droplet with diameter  $d_i$ ;  $C$  is an empirically derived entrainment coefficient which is a function of viscosity;  $E_w$  is dissipation wave energy, can be approximated from the breaking wave height;  $F_{bw}$  is fraction of sea surface covered by breaking waves which is function of wind speed. Delvigne and Sweeney did not use dispersants in their experiments.

Delvigne and Sweeney (1988) claimed that the droplet size distribution is independent of oil type, weathering state, oil layer thickness and temperature under all their experimental conditions. Johansen et al. (2015) reported that a significantly different droplet-size distribution was obtained from plunger water jet experiments than predicted by Delvigne and Sweeney's model. A recent study by Li et al. (2017) using plunging breaker experiments similar to Delvigne and Sweeney's setup, however, confirmed that Eq. 7 is valid for droplets up to 800 microns in the absence of dispersants. In the presence of dispersants, the value of  $b$  varies.

Johansen et al. (2015) revisited the correlation of Delvigne and Sweeney's model and proposed to use a modified Weber number to predict the droplet size distribution under breaking wave conditions:

$$\frac{d}{h} = AWe^{-0.6} \left[ 1 + \frac{B}{A} \left( \frac{We}{Re} \right)^{0.6} \right] \quad (9)$$

where  $d$  is characteristic droplet size;  $h$  is oil film thickness;  $We$  is Weber number  $We = \frac{\rho U^2 d}{\sigma}$ ,  $\rho$  is oil density,  $U$  is the free fall velocity from a plunger breaker,  $\sigma$  is interfacial tension;  $Re$  is Reynolds number,  $Re = \frac{\rho U d}{\mu}$ ,  $\mu$  is oil dynamic viscosity. The two coefficients  $A$  and  $B$  were obtained by fitting equation 9 to data collected from their experiments where surface oil films were impacted by plunging water jets. Johansen et al. (2013) used the same modified Weber number equation to predict the droplet-size distribution for subsurface oil jets (as might result from a subsea well blowout), however, they used a different set of empirically determined coefficients  $A$  and  $B$  (Johansen et al., 2013). Similar to Johansen's work, Li et al. (2017) and Galagan et al. (2018) proposed an equation to predict droplet size distributions resulting from dispersion of surface slicks that uses the Weber number ( $We$ ) and the Ohnesorge number ( $Oh$ ):

$$\frac{Vd_{50}}{d_0} = rOh^p We^q \quad (10)$$

where  $Vd_{50}$  is the volume mean diameter;  $d_0$  is the characteristic length scale;  $r$ ,  $p$ , and  $q$  are empirical coefficients. The three empirical coefficients were obtained by fitting the experimental data from Delvigne and Sweeney (1988), Delvigne and Hulsén (1994) and Reed et al. (2009). A major limitation of Johansen and Li-type correlations is that they only provide a characteristic diameter. The droplet size distribution has to follow certain analytical functions, such as a normal distribution, lognormal distribution, or Rossin-Ramler distribution (Karabelas, 1978; Mugele and Evans, 1951; Simmons and Azzopardi, 2001). A potential problem with fitting the

droplet size distribution using any of these functions is that it can result in droplets larger than physically stable. For example, the Rayleigh-Taylor instability maximum diameter that predicts maximum stable droplet sizes (Grace et al., 1976). These researchers have been trying to redistribute the volume above stable size to the fitted analytical functions; however, this may cause divergence in the size distribution results even with the same predicted mean diameter (Dissanayake et al., 2018). The coefficients are obtained from fitting to limited experimental data, which questions their accuracy when used outside conditions of the experimental data (Brandvik et al., 2013; Johansen et al., 2013).

Zhao et al. (2014) developed a physically based droplet size distribution (DSD) model VDROD. The major mechanisms for droplet breakup in turbulent flow is the bombardment of droplets by turbulent eddies. When energy forces induced by the fluctuating eddies exceed the resisting forces, i.e. interfacial tension and viscous effects, of the dispersed phase (e.g. oil or gas), droplets burst into smaller droplets. The VDROD model was developed to consider these mechanisms. Zhao et al. (2014) did a numerical exercise to estimate DSD of oils in breaking waves by periodically introducing a high energy input to replicate the breaking wave events, and zero energy to present the calm period after the breaking wave passes. Further studies are still needed to validate their model under a wide variety of oil types and wave conditions.

Dispersion of oil into the water column can result in large droplets that quickly resurface and may rejoin the surface slick and small droplets that remain entrained for longer periods. The subsequent transport of small oil droplets is not well understood. Lunel (1993) indicated that very small droplets (e.g. <100 microns) do not persist in the near surface. The current oil spill models often assume a cutoff droplet size, of which droplets smaller than the cutoff size do not resurface (Barker et al., 2019; Galagan et al., 2018). A recent study by Boufadel et al. (2020)

investigated the transport of oil droplets following a surface oil spill by using the vertical eddy diffusivity profile from an oceanography model. Their approach provides a physical explanation of the transport behavior of the small dispersed droplets in the water column; that is, the vertical turbulent diffusion overcomes the buoyancy of small droplets to transport them deeper into the water column.

Great efforts have been made to study the droplet formation under wave actions in recent years. The scientific community has a quite good understanding of the mechanisms of droplet formation in turbulent flows now. However, the current model predictability of droplet size distribution is still in question. More reliable experimental and field data are needed for model calibration and validation.

### **Oil Dissolution**

For surface slicks, dissolution has been considered a secondary process because most of the soluble components in oils have high partial pressures, and this results in evaporation dominating loss of these components (Galagan et al., 2018; McAuliffe, 1989; Stevens et al., 2015). Based on Raoult's law, MacKay and Leinonen (1977) developed a modeling scheme for the dissolution of surface oil slicks. The slick is treated as a flat plate, and a well-mixed oil layer is assumed with most of the resistance to mass transfer lying in a hypothetical stagnant region (boundary layer) close to the oil. The dissolution rate is expressed as (Galagan et al., 2018):

$$\frac{dN_i}{dt} = K_i [e_i x_i C_{si} - C_{wi}] A \quad (10)$$

where  $N$  is the dissolved mass, the subscript  $i$  represent oil component  $i$ ;  $e$  is an enhancement factor that is a function of temperature;  $x$  is oil phase mole fraction;  $C^s$  and  $C^w$  are the component solubility and the actual concentration of the component in the water phase, respectively;  $A$  is the surface area of slick. The mass transfer coefficient  $K_i$  is related to Sherwood number, diameter of

the surface slick, and diffusion coefficient. Eq. 10 can also be used for dispersed oil in the water column, where the surface area  $A$  can be treated as the surface area of an oil droplet. Under high energy sea state, the dissolution can be enhanced due to the continuous dispersion and droplet resurfacing process, which is closely related to the .

Dissolution becomes more important in a deep subsea oil release because volatilization can't happen and the formation of small droplets rising to the surface enhancing dissolution compared to stable surface slicks. Gros et al. (2017) predicted that 27% of the released mass of petroleum fluids from Deepwater Horizon blowouts dissolved into the sea during ascent from the wellhead to the sea surface. Detailed algorithms for dissolution in deep water will not be presented herein since it is beyond the scope of the current paper.

### **Oil Biodegradation and photo-oxidation**

Biodegradation of oil depends on the oil-water interfacial area, where the microbes can access to the substrates (Atlas and Hazen, 2011). Since the interfacial area of a slick is much smaller than the dispersed oil droplets giving the same oil volume, the biodegradation of surface slicks are considerably slower compared to the biodegradation of small droplets dispersed into the water column. Thus, oil dispersion is a key factor affecting biodegradation. The most frequently used model to estimate biodegradation rates is the first-order decay algorithm (Galagan et al., 2018). The oil can be treated as a whole or individual hydrocarbon components. Yassine et al. (2013) used a Monod kinetics and a quasi-steady state approximation for the dissolution of low solubility hydrocarbons in the water column. They reported good agreement with data. Vilcáez et al. (2013) assumed that the microorganisms covered oil droplets completely. Their model suggested that oil droplets biodegraded faster than dissolved oil



components due to their assumption of complete microbial coverage of oil droplets. However, there were no data to confirm their assumption.

Photo-oxidation occurs when crude / fuel oil are exposed to sunlight. It results in formation of polarized oxygenated compounds that can change oil interfacial properties and potentially facilitating their chemical and biological degradation (Mackay and McAuliffe, 1988). Currently, there aren't any models to predict the photo-oxidation process. Ward et al. (2018) conducted lab experiments by exposing oil films to a solar simulator for days and found that photo-oxidation changed the oil properties dramatically. We recently conducted photo-oxidation experiments in a large test tank facility in Leonardo, NJ allowing oil film exposure to natural sunlight for varying durations. We intend to use the resulting data to facilitate the model development.

### **Summary and Conclusions**

We completed a study of the major algorithms used in integrated oil spill fate and effects models in order to identify opportunities to update them based on advances in the understanding of oil behavior. In addition, we developed a prioritized list of these algorithms that could undergo updating based on the importance of the algorithm to modeling predictions and the advancement in the state of knowledge for each. The top two algorithms identified for this prioritization are water-in-oil emulsification and photo-oxidation.

We believe that upgrading emulsification algorithms is a high priority because current algorithms are based on limited experimental data and these experiments may not have been conducted using protocols that represent oil behavior in the real world. Current protocols rely on empirical correlations that may not extrapolate to field conditions that could differ significantly from the limited experimental conditions. Oil emulsification plays a critical role in oil fate and

response decision making. Because of this, we have initiated a set of workshops between oil spill modeling, response decision makers, stakeholders, and industry to develop a plan for increasing our understanding of the emulsification process and developing more robust algorithms. Our goal is to develop algorithms based on an understanding of the key physical and chemical properties of oil that influence emulsification rate and stability.

We also gave high priority to development of algorithms to predict oil photo-oxidation. This is because of advances in research that indicates photo-oxidation plays a more important role in oil behavior after a spill than previously thought and the fact that models currently don't include emulsification algorithms.

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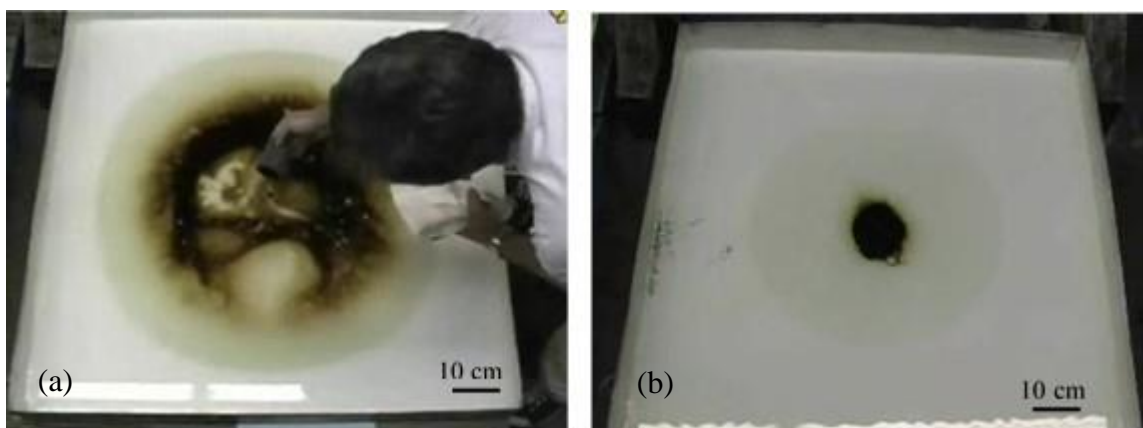


Figure 1. Oil spreading experiments conducted in a 1 m<sup>2</sup> pan. The images were taken 3.98 s after oil release: a) ANS (Alaska North Slope) crude oil with density of ~860 kg/m<sup>3</sup>, viscosity of ~10 cp, and interfacial tension of ~16 mN/m; b) high viscosity fuel oil with density of ~900 kg/m<sup>3</sup>, viscosity of ~13000 cp, and interfacial tension of ~43 mN/m. Source of the oil properties were obtained from Environmental Canada Oil and Chemical Database (Environmental Canada, 2019).

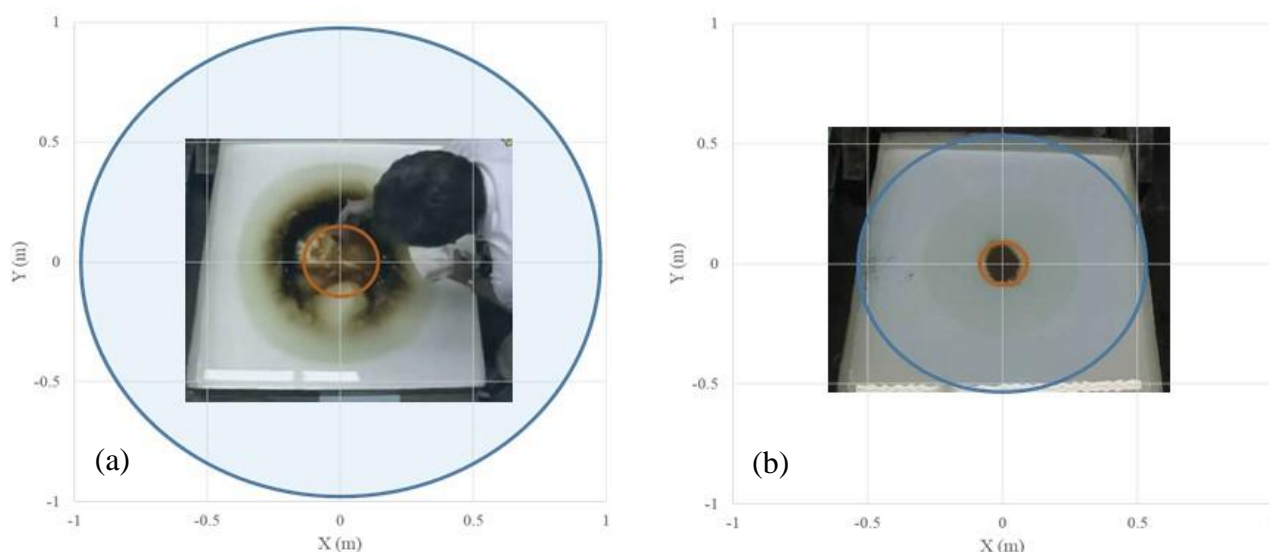


Figure 2. Predictions from Fay-Hoult's theory compared to experimental results. The predictions were obtained at 3.98 s, the same time period that the images were taken. The orange circle is generated from Fay's second stage of the spreading, and the blue circle is the third stage: a) ANS crude oil; b) high viscosity fuel oil.