Modeling Dissolution of Oil Droplets
During the Ascent in Marine Water
After a Deep Water Oil Spill

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Abstract

Deep water drilling has been growing, but the dangers of drilling in such extreme conditions became apparent with BP’s Deepwater Horizon’s blowout. Millions of gallons were released into the Gulf of Mexico, devastating the fragile wetlands around the coast and revealed gaps in how deep water blowouts needed to be addressed. Current models describe surface spills effectively, but do not take into account the effect of dissolution that has a major part in deep water spills. A theoretical Binary Solute-sink model was used to describe a dissolution of a deep water spill, and a oil droplet size distribution obtained from the Gulf of Mexico was used to evaluate the amount of oil that goes into solution and the amount of oil that reaches the surface. 22.1% of the oil released in a blowout goes into solution, and 11.6% of the oil released in a blowout goes to the surface. This leaves the majority of the oil under the sea. This model should be incorporated with ocean current and weather patterns in order to fully describe the oil spill system.

Introduction

BP’s Deepwater Horizon/Macondo Spill on April 20, 2010, was one of the most serious oil spills in U.S. history. Not only was the amount of oil released into the Gulf of Mexico a problem for the delicate wetlands surrounding the coast, but the tremendous depth at which the blowout took place presented novel complications for engineers. The wellhead was located under 1500 meters (4921 feet) of water, meaning under a pressure of about 150 bars or 150 times atmospheric pressure (1). The conditions—high depth, high pressure, low temperatures, and high volume oil release—created a blatant contrast to past spills. This spill was the first at such a depth, and it was the first in which dispersants were applied directly at the wellhead (2); a plume of hydrocarbons was also noticed at a depth of 800-1200 meters. The implications of applying dispersants at the wellhead as well as how the oil affected deep-sea organisms are largely unknown. An important step in understanding and addressing the effects to wildlife, wetlands, coastlines, and humans is in knowing the fate of the oil.

Oil Budget Models

Models for “oil’s fate” have been developed and implemented in past surface spills, but there has not been a complete model developed for deep water spills. In the Macondo spill, hot, highly turbulent, pressurized oil and gas entered cold seawater and produced a variety of dispersed phases, including oil droplets, gas bubbles, and oil-gas emulsions (3). A large hydrocarbon plume was observed at depths of 800-1200 meters; this was unique and showed how little was known about the way a spill behaves at deep depths.

It is imperative that a model look at the natural and human processes that took place in the Gulf that would have removed the oil or caused its dispersion. The Oil Budget Calculator: Deepwater Horizon
developed a model specific to a deepwater spill. It looks at multiple fates, such as evaporation, weathering, natural dispersion, chemical dispersion, burning, and mechanical recovery (4). Although dissolution is mentioned in the report, it is grouped with evaporation, and it is not given serious consideration.

This study aims to analyze the importance of dissolution in conditions present in the Macondo spill and present a theoretical model that shows the change in oil as it rises through the water column and determines the amount of oil that goes into solution.

**Dissolution**

For the Macondo Oil Spill, dissolution is when water-soluble oil components, especially low molecular weight aliphatic and aromatic hydrocarbons, dissolve in water (5). The rate of dissolution depends on concentration gradient, solvent and solute properties, temperature, and interfacial surface area. Unlike surface spills, the oil spends the majority of its time in the water, and therefore, its interaction with the water needs to be incorporated into oil fate models. An unknown amount of oil is lost into the surrounding water as the oil travels towards the surface. A simulated deep water oil spill conducted by Johansen showed that the oil slick at the surface was much thinner from a deep water spill than a slick formed by a spill closer to the surface (6). Figure 1 shows where the oil could have gone from the Macondo spill.

![Figure 1: The possible fates of the oil from the Macondo blowout (7).](image-url)
While many studies on oil dissolution have not been done, with the expansion of deep water oil exploration and drilling, it is important that this knowledge gap be filled. Hamam has looked at the crude oil dissolution in saline water, and the results of the study show the importance of temperature and salinity in the rate of dissolution (7).

Oil released in deep water blowouts break up into different sized droplets (8). The size of the droplet affects the rate of dissolution, the time it takes for the oil to reach the surface (rise velocity), the size of the slick, and the location of the oil in the water column, and thus, is an important parameter of a blowout. Difference types of blowouts can create different regimes, which produce different size distributions of droplets. Figure 2 shows the different regimes that are possible for a deep water blowout as described by Chen and Yapa (8).

Figure 2 shows a picture from Macondo at the blowout point.

Figure 3 shows a picture from Macondo at the blowout point.
Comparing Figure 2 to Figure 3, it can be seen that the Macondo spill is in the Type 3 regime or fully atomized flow. This is when there is a large and high velocity release. Literature and other researches have found that the Macondo release was in fully atomized flow (3). Although it is difficult to determine the exact oil droplet size distribution at the blowout point, methods published allow a reasonable distribution estimate that can be used in oil fate calculations (8). Field data from various depths can also be used as a reasonable estimate of the oil droplet size distribution at the blowout point. Table 1 shows how important the droplet size can be based on rise velocity; Figure 4 shows a more dramatic graphical representation of the data presented in Table 1 (4).

<table>
<thead>
<tr>
<th>Diameter (μm)</th>
<th>Rise velocity (cm/min)</th>
<th>Time to rise 1 metre (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.03</td>
<td>3330</td>
</tr>
<tr>
<td>20</td>
<td>0.132</td>
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<td>2</td>
</tr>
<tr>
<td>500</td>
<td>81.6</td>
<td>1</td>
</tr>
</tbody>
</table>

*Table 1: Rise velocity of oil droplets at various diameters (4).*

*Figure 4: The smaller diameters take really long times to rise 1 meter.*
Rise velocity ultimately determines if a droplet of oil reaches the surface or if it is basically “suspended” within the water column. In this sense, suspension is when the oil droplet rises so slowly that it will take years to rise through the entire length of the water column. These droplets are the ones that create the plume. Ultimately, the physical property of the oil droplet that determines its fate is the density.

During dissolution, the oil droplet diameter changes, so subsequently, the rise velocity changes as well. The droplet rises through the water column because the overall density of the droplet is less than that of the surrounding marine water. However, as the more soluble components leave the droplet, the density of the droplet increases. The density eventually reaches that of the surrounding water and becomes suspended. For some droplets, the diameter is so small, the droplet has a negligible rise velocity and becomes suspended at that depth. Dissolution continues, and the density increases until it reaches that of the insoluble hydrocarbon components. These droplets drop to the sea floor or slowly move in that direction. Hence, there are four different fractions of oil can be defined: (1) Floaters, those that reach the surface and form the slick; (2) Suspenders, those that move so slowly that they are suspended within a certain depth range; (3) Fallbacks/Sinkers, droplets that initially rise but then sink towards the sea floor; and (4) the oil that dissolved into the surrounding sea water.

An interesting aspect of the Macondo spill was the extremely high pressure. While liquids are incompressible, the high pressure might have a noticeable effect on the time it takes the oil droplet to reach its “critical density”. For this study, critical density has been defined as the density at which the oil droplet is equal to the surrounding marine water. Pressure is directly correlated to density, so a high pressure correlation for marine water should be included in any model for deep water blowouts.

Modeling the ascent of an oil droplet through marine water presents complex variable dependencies and certain assumptions might have to be made.

**Theoretical Model Development**

The aim of this study was to develop a model that would show the change in droplet volume and density with time and to see the amount of oil that went into solution. Thibodeaux’s Binary Solute-Sink Model was used as the model, and the model is shown below in Equation 1 (11).

\[ K^{-1}t = \int_{X(t)}^{X_0} \frac{(X(t)+1)^{1/3}}{X(t)} \, d[X(t)] \tag{Equation 1} \]

Where \( t \) is the time period (hr), \( X \) is a parameter that defines the soluble to insoluble volume ratio, and \( K \) is a parameter that describes mass transfer. \( X \) is defined in Equation 2, and \( K \) is defined in Equation 3.

\[ X(t) = \frac{\text{Volume of soluble component} \, (t)}{\text{Volume of insoluble component}} \tag{Equation 2} \]

Where the the volume of the insoluble component is assumed to be constant.

And,
\[
K \ (hr^{-1}) = \frac{6K_w(X_0 + 1)^{1/3}}{K_{ow}d_0}
\]

Equation 3

Where \(K_w\) is the mass transfer coefficient on the water side, \(X_0\) is the initial soluble to insoluble volume ratio, \(K_{ow}\) is the partitioning coefficient between oil and water, and \(d_0 \ (m)\) is the initial diameter of the oil droplet. \(K\) is also assumed to remain constant, although the mass-transfer coefficients change with volume change. The value used for \(K_w\) is 0.0004 m/hr, and the oil-water partitioning coefficient, \(K_{ow}\), was set equal to 1000. The volume ratio, \(X\), was chosen as 3 to make the density slight less than that of seawater.

This model describes a binary system (soluble and insoluble). Benzene was chosen as the representative chemical for oil’s soluble components, and orthodichlorobenzene (ODB) was chosen as the representative chemical for oil’s insoluble components. The densities of benzene and ODB were used in this analysis.

To numerically solve Equation 1, a fourth-order Runge-Kutta was applied to a modified equation. Equation 4 represents the right-side of Equation 1.

\[
Y = \int_{X(t)}^{X_0} \frac{(X(t) + 1)^{1/3}}{X(t)} \ d[X(t)]
\]

Equation 4

The Runge-Kutta was applied as such shown in Equation 5 to 10.

\[
\frac{dy}{dx} = f(x_n, y_n)
\]

Equation 5

\[
k_1 = hf(x_n, y_n)
\]

Equation 6

\[
k_2 = hf \left(x_n + \frac{1}{2} h, \ y_n + \frac{1}{2} k_1 \right)
\]

Equation 7

\[
k_3 = hf \left(x_n + \frac{1}{2} h, \ y_n + \frac{1}{2} k_2 \right)
\]

Equation 8

\[
k_4 = hf \left(x_n + h, \ y_n + k_3 \right)
\]

Equation 9

\[
y_{n+1} = y_n + \frac{1}{6} k_1 + \frac{1}{3} k_2 + \frac{1}{3} k_3 + \frac{1}{6} k_4
\]

Equation 10

Once the Runge-Kutta was completed, \(Y\) was set equal to \(K^{-1}t\), and \(t\) was solved for. This was the time that it took to reach a particular depth and also defined droplet diameter, which allowed for the determination of the amount of oil that went into dissolution. All calculations were completed on Excel.

The oil droplet distribution used was from the Macondo Oil Budget Calculator and is reproduced below (4).
<table>
<thead>
<tr>
<th>Median Particle Diameter (µm)</th>
<th>Distribution (%)</th>
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<tbody>
<tr>
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<tr>
<td>3.2</td>
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<td>122</td>
<td>4</td>
</tr>
<tr>
<td>144</td>
<td>4</td>
</tr>
</tbody>
</table>

*Table 2: Oil Droplet Size Distribution from field during Macondo Blowout*
All droplet diameters used for analysis were median values. The oil droplet distribution was obtained from the field from a depth of 0-50 meters (4).

Temperature, salinity, and pressure were all incorporated into the model using “The High Pressure International Equation of State for Seawater, 1980”, from Millero et al (10). This equation of state relates the density of seawater to salinity, temperature, and pressure. While the droplet density is assumed to be dependent only upon its components, its density can be compared to an accurate seawater density. Figure 6 shows Millero’s Equation of State for Seawater.

![Graphical representation of oil droplet size distribution from Brooks-McCall](image)

**Figure 5:** Graphical representation of oil droplet size distribution from Brooks-McCall

The density \( \rho(S,T,P) \) of seawater at high pressure is to be computed from the practical salinity \( S \), the temperature \( T \) (°C) and the applied pressure \( P \) (bars) with the following equation:

\[
\rho(S,T,P) = \frac{\rho(S,T,0)}{1 - p/K(S,T,P)}
\]

where \( \rho(S,T,0) \) is the One Atmosphere International Equation of State of Seawater, 1980, and \( K(S,T,p) \) is the secant bulk modulus given by:

\[
K(S,T,p) = K(S,T,0) + A_T p + B_T p^2
\]

where

\[
K(S,T,0) = K_w + (54.6746 - 0.603459 T + 1.09987 \times 10^{-1} T^2 - 6.1676 \times 10^{-5} T^3) S + (7.944 \times 10^{-7} + 1.6483 \times 10^{-2} T - 5.3009 \times 10^{-4} T^2) S^2/3;
\]

\[
A_T = A_w + (2.2838 \times 10^{-7} - 1.0981 \times 10^{-2} T - 1.6078 \times 10^{-6} T^2) S + 1.91075 \times 10^{-4} S^3/2;
\]

\[
B_T = B_w + (-9.3488 \times 10^{-7} + 2.0816 \times 10^{-4} T + 9.1629 \times 10^{-10} T^2) S;
\]

and the pure water terms \( K_w, A_w, \) and \( B_w \) of the secant bulk modulus are given by:

\[
K_w = 19.652211 + 148.4206 T - 2.327 \times 10^{5} T^3 + 1.360.477 \times 10^{-2} T^4 - 5.155.288 \times 10^{-4} T^5;
\]

\[
A_w = 3.239.908 + 1.437.13 \times 10^{-3} T + 1.160.92 \times 10^{-4} T^2 - 5.779.05 \times 10^{-7} T^3;
\]

\[
B_w = 8.509.35 \times 10^{-5} - 6.122.93 \times 10^{-4} T + 5.2787 \times 10^{-4} T^2
\]

The High Pressure International Equation of State for Seawater, 1980, is valid for practical salinity from 0 to 42, temperature from -2 to 40°C and applied pressure from 0 to 1000 bars.

![The High Pressure International Equation of State for Seawater](image)

**Figure 6:** The High Pressure International Equation of State for Seawater allows for the correlation between density of seawater and temperature, salinity, and pressure (10).
Temperature changes with depth, so functions based on the thermocline of the sea (Figure 7) is shown in Equations 11 and 12, and temperature is also incorporated into the model as a depth dependent variable.

\[
\begin{align*}
\text{Temperature} &= (10^{-8})\text{Depth}^3 + (8 \cdot 10^{-6})\text{Depth}^2 - 0.0446(\text{Depth}) + 29.763 \quad \text{Equation 11} \\
\text{Temperature} &= (4 \cdot 10^{-6})\text{Depth}^2 - 0.0124(\text{Depth}) + 13.986 \quad \text{Equation 12}
\end{align*}
\]

Where Temperature is in Celsius and Depth is in meters.

For a depth of 900 meters to the surface, Equation 11 was used. For a depth of 1500 meters to 900 meters, Equation 12 was used.

The depth of the oil droplet was determined by the rise velocity. A function was created relating the rise velocity versus oil droplet diameter data from the Macondo Oil Budget Calculator and was incorporated into the model (4).

The model can be used for any salinity (0-44), pressure (0-100 bar), or temperature (-2- 40 °C) within the limits noted.
**Results, Discussion, and Remarks**

Figure 8 shows a summary of the results and shows the range of particle sizes that fall into the floater, suspender, and sinker fractions.

![Graph showing depth at critical density vs. particle size](image)

Figure 8: Oil fractions with oil droplet size ranges

The suspenders are less than 16 μm, the sinkers (or fallbacks) are between 16 μm and 75 μm, and the floaters are greater than 75 μm. The general range of particle sizes and corresponding oil fractions agree with theory. Floaters have more soluble, and thus more volatile, components and fast rise velocity. Suspenders move so slowly that they remain close to or near the blowout. Sinkers initially rise but then sink once the density is greater than the surrounding seawater. The height to which the blowout propelled the droplets was not taken into account in this study. Figures 9, 10, and 11 are detailed examples of each fraction.
For an 8 µm oil droplet, the point at which the red (seawater density) and blue lines (oil droplet density) intersect is the critical density. It takes about 330 hours to reach this point; however, the droplet has only risen less than 4 meters. The droplet only continues to get smaller and slower, and thus, remains suspended. These droplets make up the plume over a depth range.
For a 40 μm oil droplet, the point at which the red and blue lines intersect is the critical density. It takes about 1550 hours to reach this point. The droplet rose to 1050 meters. Although it is still a slow ascent, this droplet has the time and the diameter to reach a larger density than seawater and fallback/sink.

![Figure 11: 100 micron oil droplet, representing the floater range](image)

For a 100 μm oil droplet, the point at which the red and blue lines intersect is the critical density. However, notice that the green line (the one than shows the change in depth) is in the negative depth region at critical density. This means that it is flying out into the atmosphere! Since this is not physically possible, this droplet reaches the surface and forms the slick.

From the summation of oil lost into dissolution for a unit volume, it was found that 22.1% of the oil released by a blowout goes into solution. The percentage of oil lost in dissolution by droplet size is shown in Figure 12.
Because the majority of the droplets from the release are around 8 μm, the majority of the oil gone into solution is from that size range.

However, the more stunning number is the percentage of oil from a blowout that reaches the surface: 11.6%. This means that 88.4% remains underwater, either in suspension, at the sea floor, or dissolved into solution.

This is a harsh reality, to know that only a tenth of the oil released was actually removed from the environment. This amount might actually be less because dispersants were sprayed at the wellhead. Dispersants make the oil droplets into smaller, which send the droplets towards the suspender or sinker ranges.

Knowing the actual amount of oil that goes into different fractions is important in mobilizing effective clean-up responses. This model should be used in conjunction with models that depict weather patterns. It would allow a more complete picture of oil's fate from a deepwater blowout.

**Future Work**

The affects of temperature and salinity on oil droplet A more representative oil droplet distribution would allow for more accurate analysis. The Excel model is made so that changes can be made simply for various conditions.
Literature Cited


Appendix

The theoretical model is an Excel program file, “Oil Droplet Dissolution Model”. It can be accessed through Dr. L. Thibodeaux or Kalpanee Gunasingha (kgunas1@gmail.com).