

# Texas A&M Oilspill Calculator (TAMOC): Modeling Suite for Subsea Spills

Scott A. Socolofsky<sup>1</sup>, Anusha L. Dissanayake<sup>1</sup>, Inok Jun<sup>1</sup>,  
Jonas Gros<sup>2</sup>, J. Samuel Arey<sup>2</sup>, and Christopher M. Reddy<sup>3</sup>

<sup>1</sup>Zachry Department of Civil Engineering, Texas A&M University  
College Station, Texas, USA  
socolofs@tamu.edu

<sup>2</sup>Environmental Chemistry Modeling Laboratory,  
Ecole Polytechnique Fédérale de Lausanne  
Lausanne, Switzerland

<sup>3</sup>Department of Marine Chemistry and Geochemistry,  
Woods Hole Oceanographic Institution  
Woods Hole, Massachusetts, USA

## Abstract

The Texas A&M Oilspill Calculator (TAMOC) is a new, freely available modeling suite for predicting fate and transport of oil and gas released from subsea accidents. The model is coded in Python and Fortran and is freely available from <http://github.com/socolofs/tamoc>. The model contains general modules for handling ambient water column data, hydrocarbon equations of state, and bubble and droplet dynamics, including particle rise velocity, shape, surface area, and heat and mass transfer rates. Three simulation models are included with the modeling suite. The Single Bubble Model (SBM) tracks the fate of a single bubble or droplet as it rises through the water column, advected by the three-dimensional ambient currents, and undergoing dissolution and heat transfer. For larger scale releases, two different integral plume models are provided. In weak currents, the Stratified Plume Model (SPM) predicts multiple subsurface intrusions; when currents are larger and the plume trajectory is deflected in the downstream direction, the suite applies the Bent Plume Model (BPM), which yields one intrusion layer and tracks separation between the released oil droplets and gas bubbles and the entrained seawater. All modeling components have been thoroughly validated to available laboratory and field data. This paper demonstrates some of the key validation metrics and applies the model to explore the dynamics of the Deepwater Horizon accident. The hot oil and gas released from the wellhead quickly cool to near ambient temperature (within 25 m above the release), and dissolution is generally faster than gas ebullition. Model predictions agree well with observations from 2010, including calculations for the depth of the intrusion layer and the flux of chemical components to the atmosphere.

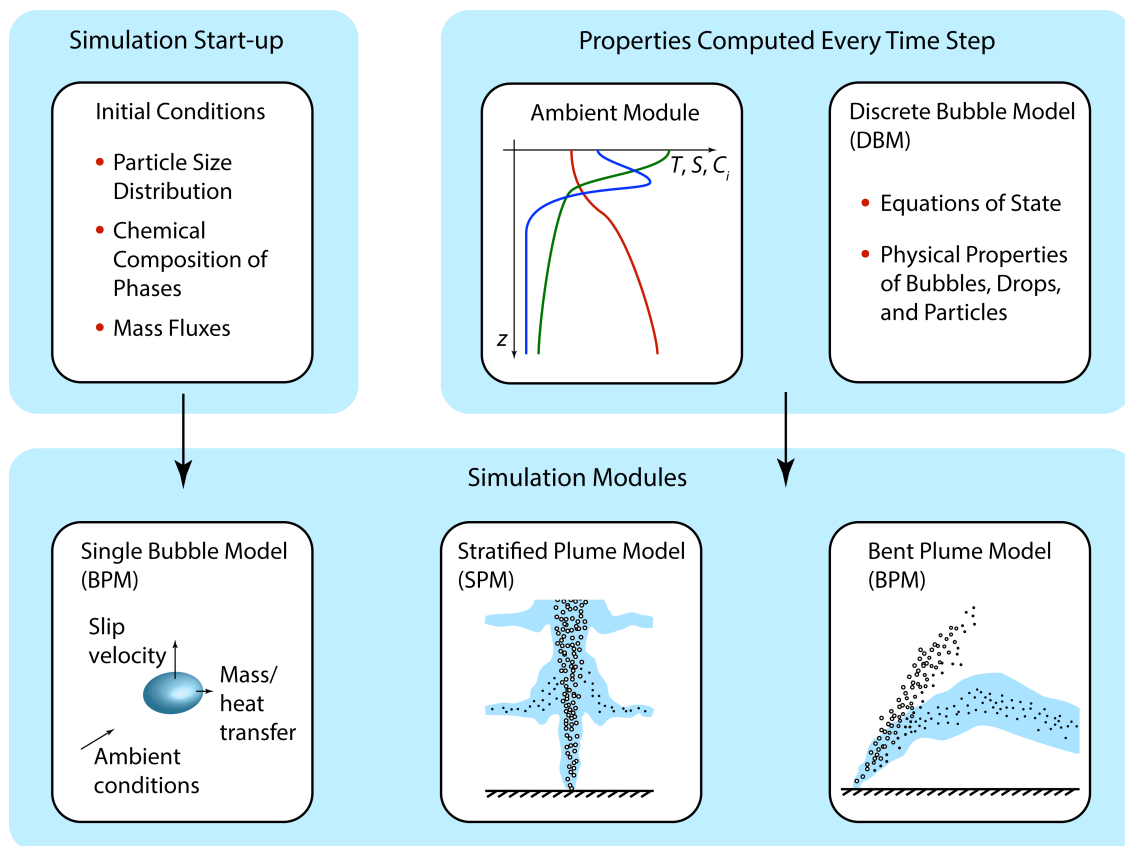
## 1 Introduction

Subsea blowouts are dramatic examples of thermodynamically active multiphase plumes, and since the Deepwater Horizon accident in 2010, many groups have been studying these dynamics with different types of models. In this paper, we present a model based on the integral approach to the multiphase dynamics (Johansen, 2003, Yapa and Zheng, 1997) and using the Peng-Robinson equation of state to consider the non-ideal oil and gas chemistry and

thermodynamics (Robinson and Peng, 1978). This model is built on the double-plume integral model by Socolofsky, et al. (2008), which stemmed from work on subsea multiphase plumes by Crouse, et al. (2007) and Wannamaker and Adams (2006). The modeling suite is flexible, including separate modules for particle and plume dynamics, making it a robust tool to study the dynamics of a range of subsea oil and gas spills.

## 2 Modeling Suite Description

The Texas A&M Oilspill Calculator (TAMOC) is a modeling suite to predict the nearfield dynamics of oil and gas released subsea in the marine environment. Figure 1 shows a schematic of the modules available in TAMOC. The model includes methods to receive boundary forcing from general circulation models of the oceans, to handle the non-ideal temperature and pressure effects on the thermodynamic properties of hydrocarbon liquids and gases, to track the heat and mass transfer from individual bubbles and droplets, and to predict the entrainment and buoyant plume effects of a blowout in a stratified and crossflowing environment. The model is coded in Python and Fortran, providing easy means for coupling individual modules of the entire simulation suite with other numerical models of breakup or ocean circulation. The model source code and documentation is available freely over the web from <http://github.com/socolofs/tamoc>.



**Figure 1 Schematic of the Modules Available in the TAMOC Suite**

**Ambient Module.** The boundary forcing in the model requires the specification of a temperature and salinity profile, and allows for input of three-dimensional currents and dissolved concentrations of trace gases and the modeled hydrocarbons. Boundary conditions are provided for a single profile assumed to be representative of the ocean dynamics at the release point. The

data can come from other numerical simulations or from measurements from a CTD or acoustic profiler.

**Discrete Bubble Model (DBM).** The heart of TAMOC's treatment of the hydrocarbon bubbles and droplets is the Discrete Bubble Model (DBM), which tracks the behavior of individual bubbles, droplets, or particles and applies their predicted dynamics to a population of identical particles along the same path. This concept was introduced for reservoir aeration plume modeling by Wüest, et al. (1992) and developed in more detail by, e.g., Bryant, et al. (2011), Little, et al. (2001), McGinnis, et al. (2004), and Singleton and Little (2006). (e.g., Bryant, et al., 2011, Little, et al., 2001, McGinnis, et al., 2004, Singleton and Little, 2006). McGinnis, et al. (2006) adapted the discrete bubble model to non-ideal gas behavior for predicting methane dissolution in the Black Sea, and their model is the basis for the thermodynamic equations of state in TAMOC, but with several extensions to cover a wide range of hydrocarbons and an enhanced equation of state.

Temperature and pressure dependent fluid properties of oil and gas are estimated from a predictive equation of state. Hydrocarbon mixtures are represented in TAMOC by their explicit composition (e.g., methane, ethane, propane, benzene, etc.) and/or by pseudo-components of groups of hydrocarbon compounds (e.g., C10-C12, to include all molecules in a mixture having 10 to 12 carbon atoms). The properties of pure compounds are constant, and are included in a database distributed with TAMOC; whereas, the properties of pseudo-components are specific to a given oil.

Properties are estimated in the DBM model in two ways: the equation of state for the thermodynamic properties of hydrocarbon mixtures (e.g., density, fugacity, solubility, viscosity, etc.) and the physical properties of a bubble or particle (e.g., slip velocity, heat and mass transfer coefficient, diameter, surface area, etc.). TAMOC uses the Peng-Robinson equation of state for density and fugacity with the 1978 correction for heavier compounds (PR78, Robinson and Peng, 1978) and applies the volume translation method for improved density estimation by Lin and Duan (2005). The temperature-dependent binary interaction coefficients in the PR78 model are computed following Privat and Jaubert (2012). Solubility is predicted by a modified Henry's law equation, with the temperature and pressure correction following King (1969) and the correction for salinity using a Setschenow salting out coefficient. The physical properties of the bubbles and droplets are taken from Clift, et al. (1978), with the exception of the mass transfer coefficient for clean, ellipsoidal bubbles, which comes from Johnson, et al. (1969).

Properties of the hydrocarbon components needed by the DBM equations (e.g., critical point properties, acentric factor, diffusivity, etc.) are taken from the literature where available or estimated using various group contribution methods. Most of the literature values of hydrocarbon properties are from Poling, et al. (2001). Missing critical-point properties and acentric factors are estimated using group contribution methods by Avaullee, et al. (1997) and Gharagheizi, et al. (2011). For missing Henry's law constants, we use the group contribution method in Hine and Mookerjee (1975). Temperature-dependent molecular diffusivity is estimated following Hayduk and Laudie (1974), which needs estimates of the LeBas molar volume. Hence, the TAMOC model contains a complete thermodynamic and physical description of hydrocarbon gas and liquid mixtures.

**Single Bubble Model.** The DBM and ambient data modules are used within each of the simulation modules in TAMOC. The simplest simulation module is the Single Bubble Model (SBM), which tracks the evolution of one bubble or droplet rising through the water column. As

in all of the simulation modules, dissolution of individual particles is computed using a Ranz-Marshall equation

$$\frac{dm_i}{dt} = -A\beta(C_s - C)_i \quad (1)$$

where  $m_i$  is the mass of an individual compound in the hydrocarbon mixture,  $A$  is the surface area of the droplet or bubble,  $\beta$  is the mass transfer coefficient,  $C_s$  is the solubility of compound  $i$  and  $C$  is the ambient concentration of compound  $i$  in the surrounding seawater. Temperature of a bubble or droplet is modeled by a similar equation for heat transfer. Transport in the SBM is computed by coupling the dissolution and heat transfer equations to an advection equation

$$\frac{d\vec{x}}{dt} = \vec{u} + u_s \hat{k} \quad (2)$$

where  $\vec{x}$  is the vector position of the particle,  $\vec{u}$  is the vector velocity of the ambient seawater, and  $u_s$  is the slip velocity of the bubble or droplet relative to the ambient seawater, taken in the vertical direction  $\hat{k}$ . In the oceans, this type of particle dynamics may occur for very weak flares rising from a natural seep or for small oil droplets rising out of the intrusion layer formed by an accidental oil well blowout.

**Integral Plume Models.** In the case of a blowout, the large release of oil and gas at a localized point gives rise to a buoyant plume, similar in character to wastewater outfall plumes, but modified by the multiphase nature of the oil droplets and gas bubbles. TAMOC handles these cases using two different simulation modules: the Stratified Plume Model (SPM) and Bent Plume Model (BPM). These integral models solve for the cross-sectionally averaged quantities of flow rate, momentum flux, and buoyancy flux by solving a set of conservation equations for mass, momentum, and buoyancy.

When ambient currents are small, the stratification dominates the flow, and several subsurface intrusion layers may form. For example, at least two subsurface intrusions were observed below 800 m depth for the Deepwater Horizon (Spier, et al., 2013). To simulate these dynamics, TAMOC applies the SPM, which uses an Eulerian double-plume integral model (e.g., Asaeda and Imberger, 1993; Crouse, et al., 2007; Lemckert and Imberger, 1993; Socolofsky, et al., 2008) to predict several intrusion layers. The model has an inner, rising plume of oil, gas, and entrained seawater, and an outer, annular downdraught plume of intruding hydrocarbon-enriched seawater. Bubbles and droplets are tracked through the model using the DBM approach, predicting their dissolution and thermodynamic evolution as they rise. The dynamics equations for the SPM were presented and validated in Socolofsky, et al. (2008). In TAMOC, this model is generalized to allow multiple dispersed phase particles by summing the void fraction and buoyant force for each particle in the simulation and to provide the more comprehensive equations of state.

In stronger currents, the blowout plume bends over in the downstream direction, and gas bubbles and larger oil droplets may rise out of the upstream edge of the plume (e.g., Socolofsky and Adams, 2002). For these plumes, TAMOC applies the BPM, which uses a Lagrangian integral plume approach, similar to most other blowout plume models (e.g., Chen and Yapa, 2004; Johansen, 2003; Johansen, et al., 2003; Yapa and Chen, 2004; Yapa and Zheng, 1997; Yapa, et al., 2001; Zheng and Yapa, 1998; Zheng, et al., 2003). The BPM computes the deformation of the plume centerline by the ambient currents, predicts separation between the dispersed phase particles and the entrained seawater, and the entrained water comes to rest at a

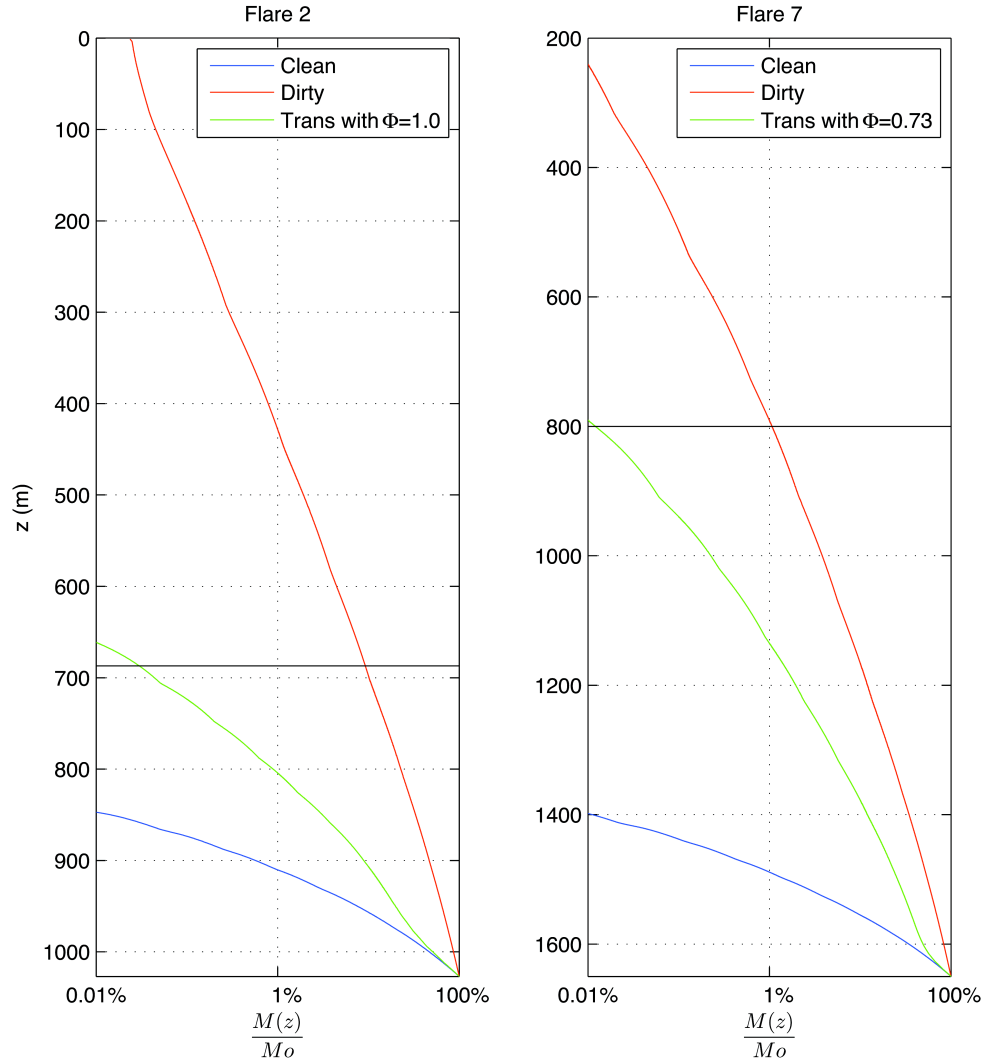
single intrusion level. The model in TAMOC follows the Lagrangian equations in JETLAG (Cheung and Lee, 1996; Cheung and Lee, 1999; Lee and Cheung, 1990) with an improved entrainment formulation from CorJet (Jirka, 2004) and an algorithm to track the bubbles and droplets inside the plume similar to that described in Johansen (2003).

**Treatment of Hydrate Effects.** At appropriate temperature and pressure, certain hydrocarbon molecules form clathrate hydrates with the ambient seawater. In TAMOC, a model of gas dissolution in the presence of hydrate skins has been developed that depends on the temperature difference between the hydrate dissociation temperature and the ambient temperature, called the hydrate sub-cooling. Within the hydrate stability zone, bubbles are assumed to dissolve initially at rates equivalent to that for clean bubbles. After a hydrate formation time  $t^*$ , the mass transfer rates are assumed to reduce to that of dirty bubbles. For hydrate sub-cooling less than 11°C, the hydrate formation time depends only on the bubble diameter. For hydrate sub-cooling greater than 11°C, the hydrate skin formation time is accelerated, and the reduction in the formation time ( $\phi$  between zero and 1) is proportional to the sub-cooling. The transition time correlations were calibrated by matching the measured data in Rehder, et al. (2009) for pure methane bubbles tracked with a remotely operated vehicle. The hydrate formation time scales calibrated to that data also agree well with laboratory measurements by Warzinski, et al. (2014).

### 3 Model Validation

Each of the modules within the TAMOC suite have been thoroughly tested and validated to available data. The equation of state and particle properties in the DBM have been mostly tested by comparison to example data provided with each of the equations implemented in the model. The SBM has also been validated for idealized cases (e.g., inert particles) to analytical solutions to the model equations. Moreover, validation of the SPM was presented in Socolofsky, et al. (2008). In this section we present validation of the hydrate effects methods and the new BPM.

**Natural Gas Seep Flares.** To validate the treatment of hydrate effects in TAMOC, we apply the SBM to predict the rise of gas bubbles from natural seeps in the oceans. For this validation, we have compared to results reported in McGinnis, et al. (2006) and in Romer, et al. (2012). These authors present the height of rise of natural gas flares measured by acoustic backscatter from shipboard depth sounders or multibeam. In both cases, the model predicts well the measured rise heights. Figure 2 shows a sample calculation for two natural seep flares reported in Romer, et al. (2012). Flare 2 originates within the hydrate stability zone, but with sub-cooling less than 11°C. The three model predictions in the figure are for simulations using clean bubble mass transfer for the whole rise time (lower, blue line), the dirty bubble mass transfer for the whole rise time (upper, red line), and the new model, where the bubbles dissolve at clean bubble rates until a transition time is reached, after which they dissolve at dirty bubble rates (middle, green line). The rise height for each flare reported in the paper is given by the horizontal black line. Flare 7 originated with hydrate sub-cooling greater than 11°C, and our calibrated model predicts the transition time to be 73% of the normal time. The gas bubble size distribution for each seep was reported in the Romer et al. (2012) paper, and the simulations in Figure 2 give the sum of the simulation results for 1000 bubbles sampled from the measured size distributions.



**Figure 2 Prediction of Natural Gas Seeps Reported in Romer, et al. (2012)**

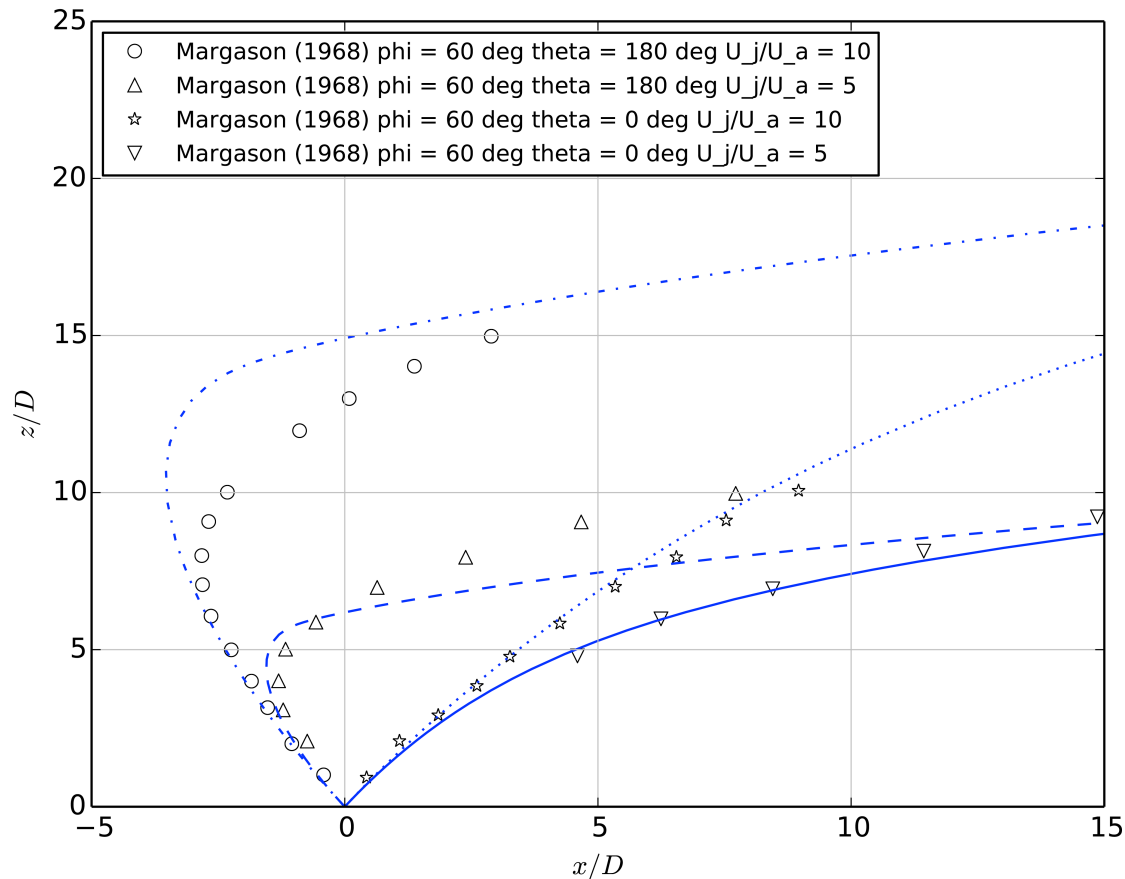
The hydrate effects prediction given by the green line matches the measured rise height very well for both seep flares. If the clean bubble mass transfer is used, bubbles fully dissolve well below the predicted rise height. On the other hand, the dirty bubble mass transfer rate is too slow, with the model predicting up to 30% of the mass rising above the measured flare height. Similar behavior and levels of agreement are seen for the other flares in the Romer et al. (2012) paper and for data in McGinnis et al. (2006).

**Bent Plume Model.** The BPM can be run either as a single-phase buoyant jet or a multiphase plume. In its form as a single-phase model, it should behave similarly to the Lagrangian JETLAG model and Eulerian CORMIX model, two mainstream buoyant jet models for wastewater outfalls. Thus, we have validated the BPM in this mode to many of the tests in Lee and Cheung (1990) and in Jirka (2004). For each test, the BPM performs with very similar fidelity to JETLAG and CORMIX.

One of the major challenges for the Lagrangian model as presented in the papers by Lee and Cheung (1990), Cheung and Lee (1996) and Lee and Chu (2003) is how to handle the combination of shear entrainment resulting from eddies inside the plume engulfing ambient

water and the forced entrainment of water flowing into the plume by the currents along the upstream side. Near the source, the shear entrainment dominates. As the plume rises, decelerates, and begins to bend over in the downstream direction, the forced entrainment begins to dominate. Several algorithms to handle this transition are presented in the literature. The main problem appears to be related to the prediction of the entrainment rate when the plume densimetric Froude number becomes small and when the plume fluid transitions from positively to negatively buoyant, as occurs in a stratified ambient. For the BPM, we use the entrainment hypothesis in Jirka (2004), which takes a linear transition between the asymptotic values for a positively and negatively buoyant pure plume. This entrainment model also seems to solve several of the shear to forced entrainment problems noted by the JETLAG papers.

The performance of this improved model is illustrated in Figure 3, showing an example calculation with the BPM for jets at oblique angles into and against crossflow. In the figure  $\Phi$  is the angle from the vertical,  $\theta$  the angle with the  $x$ -axis,  $U_j$  is the jet exit velocity,  $U_a$  is the ambient current velocity,  $D$  is the orifice diameter, and  $x$  and  $z$  are the horizontal and vertical coordinate. The symbols give the jet centerline position from laboratory experiments; the various lines show the centerline of the BPM simulation. Though the agreement is not perfect, it matches or outperforms the agreement by both JETLAG and CORMIX. Hence, the jet integral model and entrainment formulation in the BPM performs at a level similar to mainstream models in the single-phase literature.

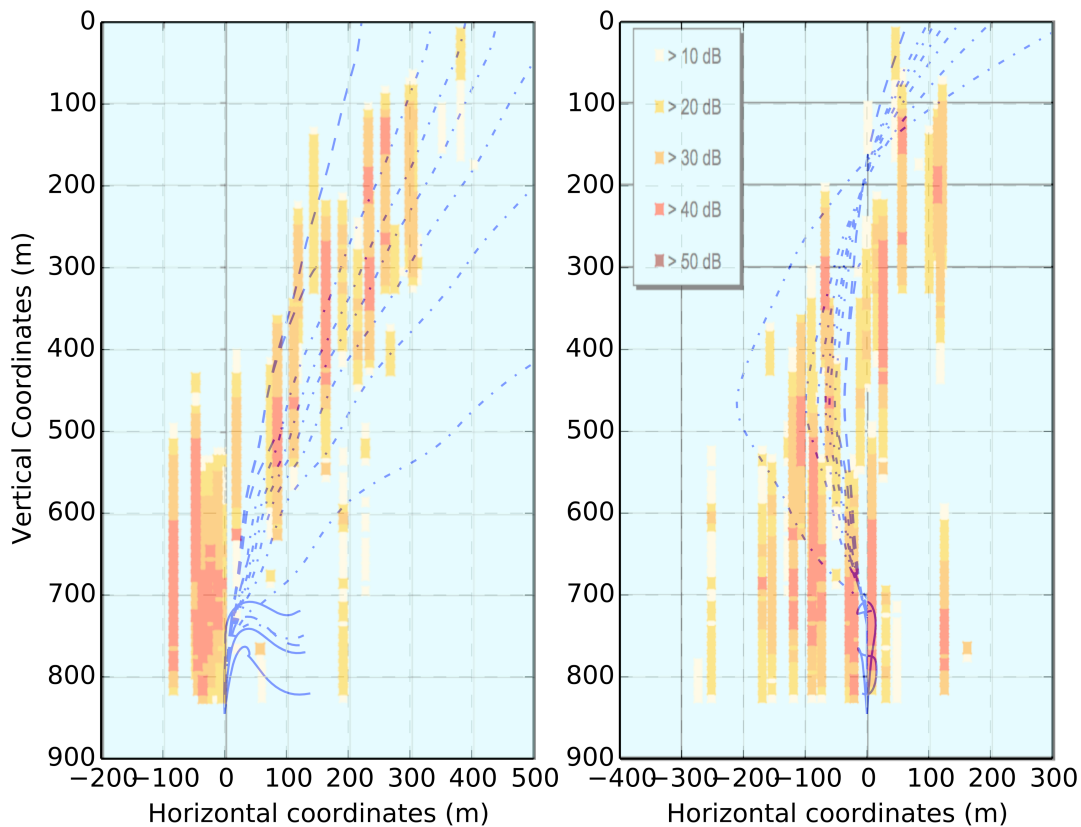


**Figure 3 Validation of BPM for Jets in Crossflow**

For a multiphase plume, two main changes have to be included in the BPM equations.

First, the buoyant force of the bubbles must be added to the momentum equation. Second, there must be means to track particles in the plume and remove their buoyancy if they rise out of the plume of entrained seawater. We add the buoyant force for the bubbles following the same equations as in Socolofsky, et al. (2008), but adapted from the Eulerian reference frame to the Lagrangian frame. Particle tracking is implemented similarly to that in the DeepBlow model (Johansen, 2003), with the plume equation integration and particle tracking occurring in series for each time step of the model. The main validation datasets are those published in Socolofsky and Adams (2002) for laboratory experiments and in Johansen, et al. (2003) for the DeepSpill field experiment.

Figure 4 shows a sample validation of the BPM to the DeepSpill experiment for a case of natural gas and crude oil mix released into seawater. The model was initialized with the flow rates and gas bubble and oil droplet size distribution reported in the DeepSpill report; currents are from a mooring that measured the velocity field during the experiments. The orange colors in the figure give the acoustic backscatter intensity measured from a shipboard depth sounder during the experiment. The solid blue line shows the nearfield plume simulation of the BPM, and the various dotted and dash-dot lines show the trajectories of different sizes of oil droplets and gas bubbles tracked by the model. As evident in the figure, the plume traps at about 740 m depth and forms an intrusion. Most of the oil droplets leave the plume at the height of maximum rise (about 710 m depth). After bubbles and droplets leave the BPM simulation, they are tracked to the surface using the SBM. The trajectories of the particle paths predicted by TAMOC are in good agreement with the acoustic data. This validation also illustrates how multiple modules of TAMOC can be used together to simulate a single subsea release.



**Figure 4 TAMOC Simulation of a Crude Oil Release from the DeepSpill Experiment**



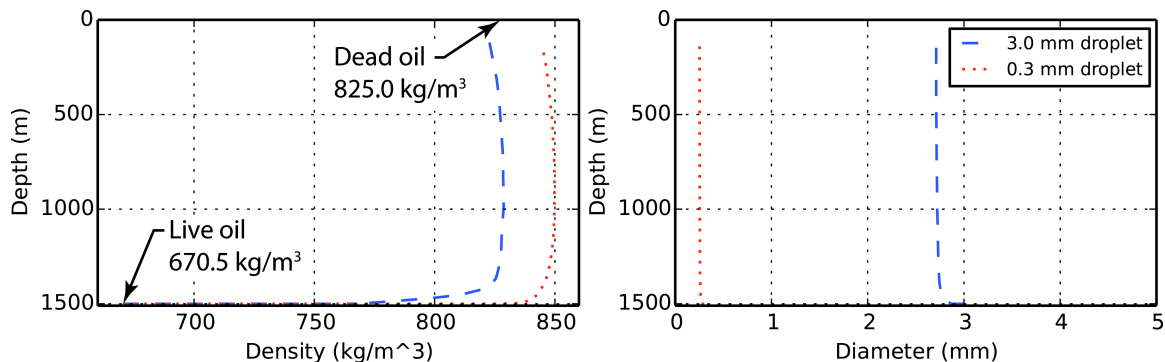
#### 4 Deepwater Horizon Simulations

As an application of the TAMOC modeling suite, we show a few results for simulations related to the Deepwater Horizon accident. These results illustrate the kinds of problems that can be studied with TAMOC and some of the important aspects of a deepwater simulation that should be considered.

**Equation of State for the Oil.** We developed a model for the Deepwater Horizon oil in TAMOC using the composition data in Reddy, et al. (2011) and a new pseudo-component model based on the GC×GC chromatogram of the oil. The model includes 279 individual components and pseudo components to describe the oil which allows TAMOC to track the detailed composition and dissolution of each of these components from a gas bubble or oil droplet. The model predicts a dead oil density at equilibrium at surface conditions of  $825 \text{ kg/m}^3$ , in good agreement with the properties reported in Reddy, et al. (2011).

**Single Bubble Model.** The simplest simulation to perform using TAMOC is to release a single droplet of oil and track its rise and chemical evolution through the water column using the SBM. This simulation is not representative of the dynamics during the blowout, but does show important characteristics of the oil and dissolution process without the complicating factors of a dynamic plume. Several authors have estimated the probable size of oil droplets coming from the Deepwater Horizon blowout (Johansen, et al., 2013; North, et al., 2011; North, et al., 2015; Ryerson, et al., 2011; Ryerson, et al., 2012; Zhao, et al., 2014a; Zhao, et al., 2014b). The general consensus is that droplets were of 1 to 10 mm scale before dispersants were applied subsea and of 0.1 to 1 mm scale with the application of dispersants. Here, we present results for a 3 mm and 0.3 mm droplet of live oil rising from 1500 m depth.

Figure 5 show the evolution of the density and the diameter of each droplet during their ascent from 1500 m depth using a CTD profile from the *R/V Brooks McCall* for the Gulf of Mexico from May 30, 2010 near the Deepwater Horizon accident. Each droplet of oil is initialized with a composition in equilibrium with the gas phase at pressures at the wellhead at  $150^\circ\text{C}$ . Due to the large amount of light components dissolved in the oil, both droplets start at a density of  $670.5 \text{ kg/m}^3$ . The smaller droplet experiences more rapid heat transfer and dissolution with height owing to its higher surface area to volume ratio and slower rise velocity. As a result, both droplets evolve to a different composition, and the properties of each droplet, specifically their density as illustrated here, are significantly different. In this comparison, the smaller droplet remains heavier than the larger droplet over its entire rise through the water column.



**Figure 5 Evolution of a 3.0 and 0.3 mm Droplet of Deepwater Horizon Oil during Ascent**

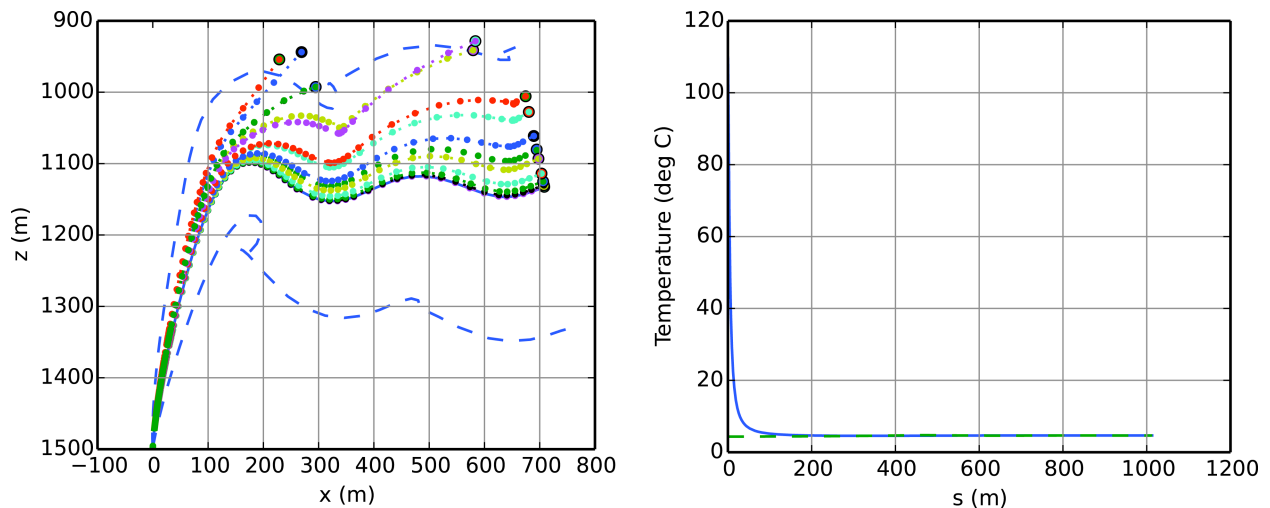
These results underscore the importance of tracking the chemical composition of each

bubble and droplet in a blowout simulation separately. Because each sized particle will have a different mass transfer rate, their compositions rapidly diverge from that of other sized particles. Once their compositions become different, then the solubility of each compound in the mixture also changes. Hence, it is necessary to compute the dissolution and heat transfer of each size of bubble or droplet separately rather than to assume all bubbles and droplets maintain the same composition with height.

**Bent Plume Model.** As a further illustration, we compute the BPM for May 30, 2010 for the Deepwater Horizon blowout. The oil and gas are initialized at equilibrium at ambient pressure and 150°C. The gas bubbles and oil droplets are sampled from a Rosin-Rammler distribution with median diameter of 5 mm and 1 mm, respectively and with spread parameters given by Johansen, et al. (2013). 10 size bins of gas bubbles and oil droplets were included, with the distribution truncated for bubble or droplet sizes larger than the maximum stable fluid particle size in Clift, et al. (1978). We use the same CTD profile from May 30, 2010 as was used in the SBM example of the previous section. The currents are assumed to be constant over the depth at 9.5 cm/s, similar to that reported in Camilli, et al. (2010).

Figure 6 presents a cross-section through the plume simulation (left) and the temperature of seawater entrained into the plume (right). The dashed line for the plume cross-section shows the edge of the Lagrangian plume element; the dotted lines show the tracks of gas bubbles and oil droplets within the plume. The intrusion level of the plume is centered just below 1100 m depth, with several of the small oil droplets following the seawater into the intrusion. The total width of the intrusion is between 200 and 300 m. Some of the larger oil droplets and gas bubbles are also seen to rise out of the top of the intrusion.

This figure also illustrates how particle can be passed from the nearfield plume simulation to a farfield particle tracking model. Each particle at the end of its path has a position, number flux, size, and complete composition description. These data can be easily provided to Lagrangian models for tracking in the farfield.



**Figure 6 BPM Simulation of the Deepwater Horizon**

The temperature inside the plume (Figure 6, right) also demonstrates the high amount of entrainment and rapid cooling of the hot oil and gas. The dashed horizontal line gives the ambient temperature;  $s$  is the coordinate along the plume centerline. The entrained fluids rapidly heat up to a maximum of 111°C within less than a meter downstream of the orifice. The plume

then cools back to ambient within just over 100 m downstream of the release, with most of the cooling occurring in less than 30 m downstream. This rapid cooling will be felt immediately by the oil and gas in the plume. Hence, the great majority of the rise of the oil and gas in a blowout will be at close to the ambient seawater temperature.

## 5 Conclusions

In this paper we have introduced the new subsea oil and gas simulation suite, TAMOC. The model has a robust physical, chemical, and thermodynamic treatment for hydrocarbon fluids and allows for simulations of a single bubble or droplet or an integral plume of blowout fluids. The model has been validated to available data in the literature, demonstrating skill on par with similar models based on the integral approach.

Application of the model to simulation the Deepwater Horizon is expected to uncover many of the complicated fluid and chemical dynamics that occurred during the spill. Here, we have illustrated only a few aspects. Using the SBM, we illustrated the importance of treating the composition of each particle size in the distribution of gas bubbles and oil droplets separately due the differential dissolution that occurs for each particle. Using the BPM, we also showed the model's skill to predict the dominant intrusion layer that occurred during the Deepwater Horizon, and demonstrated that the temperature inside the plume is expected to be close to ambient temperature for most of the plume rise.

Through these and its other modules, the TAMOC model is a robust nearfield modeling suite. This model is currently being used to couple with several farfield particle tracking models, including the General NOAA Operational Modeling Environment (GNOME), the Lagrangian Transport (LTRANS) model, and the Connectivity Modeling System (CMS). These application of these models to the data available from the Deepwater Horizon accident, we expect to further validate the model and understand the key fluid and chemical dynamics controlling the fate of hydrocarbons released by accidental subsea spills.

## 6 Acknowledgements

This work was made possible in part by a grant from the BP/Gulf of Mexico Research Initiative through the C-IMAGE and DEEP-C Consortia, grants from the U.S. National Science Foundation, grant numbers CBET-1034112, OCE-0960841, and EAR-0950600, and by a BSEE/NOAA Interagency Agreement, number E13PG00049—Answering the Challenge of Arctic Conditions.

## 7 References

Asaeda, T., and Imberger, J., "Structure of Bubble Plumes in Linearly Stratified Environments." *Journal of Fluid Mechanics*, 249: 35-57, 1993.

Avaullee, L., Trassy, L., Neau, E., and Jaubert, J.-N., "Thermodynamic Modeling for Petroleum Fluids I. Equation of State and Group Contribution for the Estimation of Thermodynamic Parameters of Heavy Hydrocarbons." *Fluid Phase Equilibria*, 139: 155-170, 1997.

Bryant, L. D., Gantzer, P. A., and Little, J. C., "Increased Sediment Oxygen Uptake Caused by Oxygenation-Induced Hypolimnetic Mixing." *Water Research*, 45: 3692-3703, 2011.

Camilli, R., Reddy, C. M., Yoerger, D. R., Van Mooy, B. A. S., Jakuba, M. V., Kinsey, J. C., McIntyre, C. P., Sylva, S. P., and Maloney, J. V., "Tracking Hydrocarbon Plume Transport and Biodegradation at Deepwater Horizon." *Science*, 330(6001): 201-204, 2010.

Chen, F. H., and Yapa, P. D., "Modeling Gas Separation From a Bent Deepwater Oil and Gas Jet/Plume." *J. Marine Syst.*, 45(3-4): 189-203, 2004.

Cheung, V., and Lee, J. H. W., "Improved Prediction of Bending Plumes - Discussion." *J. Hydraul. Res.*, 34(2): 260-262, 1996.

Cheung, V., and Lee, J. H. W., "Simulation of Oil Spills From Underwater Accidents I: Model Development - Discussion." *J. Hydraul. Res.*, 37(3): 425-429, 1999.

Clift, R., Grace, J., and Weber, M. E., *Bubbles, Drops, and Particles*, Dover Publications, Inc., Mineola, New York, 200, 1978.

Crouse, B. C., Wannamaker, E. J., and Adams, E. E., "Integral Model of a Multiphase Plume in Quiescent Stratification." *J. Hydraul. Eng-Asce*, 133(1): 70-76, 2007.

Gharagheizi, F., Eslamimanesh, A., Mohammadi, A. H., and Richon, D., "Determination of Critical Properties and Acentric Factors of Pure Compounds Using the Artificial Neural Network Group Contribution Algorithm." *Journal of Chemical and Engineering Data*, 56: 2460-2476, 2011.

Hayduk, W., and Laudie, H., "Prediction of Diffusion Coefficient for Nonelectrolytes in Dilute Aqueous Solutions." *American Institute of Chemical Engineers Journal*, 20(3): 611-615, 1974.

Hine, J., and Mookerjee, P. K., "The Intrinsic Hydrophilic Character of Organic Compounds. Correlations in Terms of Structural Contributions." *Journal of Organic Chemistry*, 40(3): 292-298, 1975.

Jirka, G. H., "Integral Model for Turbulent Buoyant Jets in Unbounded Stratified Flows. Part I: Single Round Jet." *Environ. Fluid Mech.*, 4(1): 1-56, 2004.

Johansen, O., "Development and Verification of Deep-Water Blowout Models." *Mar. Pollut. Bull.*, 47(9-12): 360-368, 2003.

Johansen, O., Brandvik, P. J., and Farooq, U., "Droplet Breakup in Subsea Oil Releases - Part 2: Predictions of Droplet Size Distributions With and Without Injection of Chemical Dispersants." *Mar. Pollut. Bull.*, 73(1): 327-335, 2013.

Johansen, O., Rye, H., and Cooper, C., "DeepSpill - Field Study of a Simulated Oil and Gas Blowout in Deep Water." *Spill Sci. Technol. B.*, 8(5-6): 433-443, 2003.

Johnson, A. I., Besik, F., and Hamielec, A. E., "Mass Transfer From a Single Rising Bubble." *The Canadian Journal of Chemical Engineering*, 47: 559-564, 1969.

King, M. B., *Phase Equilibrium in Mixtures*, Elsevier, New York., 400, 1969.

Lee, J. H. W., and Cheung, V., "Generalized Lagrangian Model for Buoyant Jets in Current." *Journal of Environmental Engineering-Asce*, 116(6): 1085-1106, 1990.

Lee, J. H. W., and Chu, V. H., *Turbulent Jets and Plumes: A Lagrangian Approach*, Kluwer Academic Publishers Group, Dordrecht, The Netherlands, 150, 2003.

Lemckert, C. J., and Imberger, J., "Energetic Bubble Plumes in Arbitrary Stratification." *J. Hydraul. Eng-Asce*, 119(6): 680-703, 1993.

Lin, H., and Duan, Y.-Y., "Empirical Correction to the Peng–Robinson Equation of State for the Saturated Region." *Fluid Phase Equilibria*, 233(2): 194-203, 2005.

Little, J. C., McGinnis, D. F., and Iwa, I. W. A., "Hypolimnetic Oxygenation: Predicting Performance Using a Discrete-Bubble Model." *Water Science & Technology: Water Supply, Vol 1, No 4*, I W a Publishing, London, 185-191, 2001.

McGinnis, D. F., Greinert, J., Artemov, Y., Beaubien, S. E., and Wuest, A., "Fate of Rising Methane Bubbles in Stratified Waters: How Much Methane Reaches the Atmosphere?" *J. Geophys. Res-Oceans*, 111(C9): 15, 2006.

McGinnis, D. F., Lorke, A., Wuest, A., Stockli, A., and Little, J. C., "Interaction Between a Bubble Plume and the Near Field in a Stratified Lake." *Water Resour. Res.*, 40(10): 11, 2004.

North, E. W., Adams, E. E., Schlag, Z., Sherwood, C. R., He, R., and Socolofsky, S. A., "Simulating Oil Droplet Dispersal from the Deepwater Horizon Spill With a Lagrangian Approach." *Monitoring and Modeling the Deepwater Horizon Oil Spill: A Record-Breaking Enterprise*, American Geophysical Union, 217-226, 2011.

North, E. W., Adams, E. E., Thessen, A. E., Schlag, Z., He, R., Socolofsky, S. A., Masutani, S. M., and Peckham, S. D., "The Influence of Droplet Size and Biodegradation on the Transport of Subsurface Oil Droplets During the Deepwater Horizon Spill: A Model Sensitivity Study." *Environmental Research Letters*, 10(2): 024016, 2015.

Poling, B. E., Prausnitz, J. M., and O'Connell, J. P., *The Properties of Gases and Liquids*, McGraw Hill, 550, 2001.

Privat, R., and Jaubert, J.N., "Addition of the Sulfhydryl Group (-SH) to the PPR78 Model: Estimation of Missing Group-Interaction Parameters for Systems Containing Mercaptans and Carbon Dioxide or Nitrogen or Methane, From Newly Published Data." *Fluid Phase Equilibria*, 334: 197-203, 2012.

Reddy, C. M., Arey, J. S., Seewald, J. S., Sylva, S. P., Lemkau, K. L., Nelson, R. K., Carmichael, C. A., McIntyre, C. P., Fenwick, J., Ventura, G. T., Van Mooy, B. A. S., and

Camilli, R., "Composition and Fate of Gas and Oil Released to the Water Column During the Deepwater Horizon Oil Spill." *Proceedings of the National Academy of Sciences*, 109(50): 20229-20234, 2012.

Rehder, G., Leifer, I., Brewer, P. G., Friederich, G., and Peltzer, E. T., "Controls on Methane Bubble Dissolution Inside and Outside the Hydrate Stability Field From Open Ocean Field Experiments and Numerical Modeling." *Marine Chemistry*, 114(1-2): 19-30, 2009.

Robinson, D. B., and Peng, D. Y., "The Characterization of the Heptanes and Heavier Fractions for the GPA Peng-Robinson Programs, ." RR-28, Gas Processors Association, 1978.

Romer, M., Sahling, H., Pape, T., Bohrmann, G., and Spiess, V. (2012). "Quantification of Gas Bubble Emissions From Submarine Hydrocarbon Seeps at the Makran Continental Margin (Offshore Pakistan)." *J. Geophys. Res-Oceans*, (1978–2012), 117(C10): 2012.

Ryerson, T. B., Aikin, K. C., Angevine, W. M., Atlas, E. L., Blake, D. R., Brock, C. A., Fehsenfeld, F. C., Gao, R.-S., Gouw, J. A. d., Fahey, D. W., Holloway, J. S., Lack, D. A., Lueb, R. A., Meinardi, S., Middlebrook, A. M., Murphy, D. M., Neuman, J. A., Nowak, J. B., Parrish, D. D., Peischl, J., Perring, A. E., Pollack, I. B., Ravishankara, A. R., Roberts, J. M., Schwarz, J. P., Spackman, J. R., Stark, H., Warneke, C., and Watts, L. A., "Atmospheric Emissions from the Deepwater Horizon Spill Constrain Air-Water Partitioning, Hydrocarbon Fate, and Leak Rate." *Geophys Res Lett*, 38, L07803, 2011.

Ryerson, T. B., Camilli, R., Kessler, J. D., Kujawinski, E. B., Reddy, C. M., Valentine, D. L., Atlas, E., Blake, D. R., de Gouw, J., Meinardi, S., Parrish, D. D., Peischl, J., Seewald, J. S., and Warneke, C., "Chemical Data Quantify Deepwater Horizon Hydrocarbon Flow Rate and Environmental Distribution." *Proceedings of the National Academy of Sciences*, 109(50): 20246-20253, 2012.

Singleton, V. L., and Little, J. C., "Designing Hypolimnetic Aeration and Oxygenation Systems - A Review." *Environ. Sci. Technol.*, 40(24): 7512-7520, 2006.

Socolofsky, S. A., and Adams, E. E., "Multi-Phase Plumes in Uniform and Stratified Crossflow." *J Hydraul Res*, 40(6): 661-672, 2002.

Socolofsky, S. A., Bhaumik, T., and Seol, D. G., "Double-Plume Integral Models for Near-Field Mixing in Multiphase Plumes." *J. Hydraul. Eng.-ASCE*, 134(6): 772-783, 2008.

Spier, C., Stringfellow, W. T., Hazen, T. C., and Conrad, M., "Distribution of Hydrocarbons Released During the 2010 MC252 Oil Spill in Deep Offshore Waters." *Environ. Pollut.*, 173: 224-230, 2013.

Wannamaker, E. J., and Adams, E. E., "Modeling Descending Carbon Dioxide Injections in the Ocean." *J Hydraul Res*, 44(3): 324-337, 2006.

Warzinski, R. P., Lynn, R., Haljasmaa, I., Leifer, I., Shaffer, F., Anderson, B. J., and Levine, J. S., "Dynamic Morphology of Gas Hydrate on a Methane Bubble in Water: Observations and New Insights for Hydrate Film Models." *Geophys Res Lett*, 41(19): 2014GL061665, 2014.

Wüest, A., Brooks, N. H., and Imboden, D. M., "Bubble Plume Modeling for Lake Restoration." *Water Resour Res*, 28(12): 3235-3250, 1992.

Yapa, P. D., and Chen, F. H., "Behavior of Oil and Gas from Deepwater Blowouts." *J. Hydraul. Eng.-ASCE*, 130(6): 540-553, 2004.

Yapa, P. D., and Zheng, L., "Simulation of Oil Spills from Underwater Accidents .1. Model Development." *J. Hydraul. Res.*, 35(5): 673-687, 1997.

Yapa, P. D., Zheng, L., and Chen, F. H., "A Model for Deepwater Oil/Gas Blowouts." *Mar. Pollut. Bull*, 43(7-12): 234-241, 2001.

Zhao, L., Boufadel, M. C., Socolofsky, S. A., Adams, E., King, T., and Lee, K., "Evolution of Droplets in Subsea Oil and Gas Blowouts: Development and Validation of the Numerical Model VDROD-J." *Mar. Pollut. Bull*, 83(1): 58-69, 2014a.

Zhao, L., Torlapati, J., Boufadel, M. C., King, T., Robinson, B., and Lee, K., "VDROD: A Comprehensive Model for Droplet Formation of Oils and Gases in Liquids - Incorporation of the Interfacial Tension and Droplet Viscosity." *Chemical Engineering Journal*, 253(0): 93-106, 2014b.

Zheng, L., and Yapa, P. D., "Simulation of Oil Spills from Underwater Accidents. 2. Model Verification." *J. Hydraul. Res.*, 36(1): 117-134, 1998.

Zheng, L., Yapa, P. D., and Chen, F. H., "A Model for Simulating Deepwater Oil and Gas Blowouts - Part I: Theory and Model Formulation." *J. Hydraul. Res.*, 41(4): 339-351, 2003.