



# Modeling atmospheric volatile organic compound concentrations resulting from a deepwater oil well blowout – Mitigation by subsea dispersant injection



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## ABSTRACT

The atmospheric concentrations of volatile organic compounds (VOCs) generated by surface slicks during an oil spill have not been extensively studied. We modeled oil transport and fate, air emissions, and atmospheric dispersion of VOCs from a hypothetical deepwater well blowout in De Soto Canyon of the Gulf of Mexico assuming no intervention and use of SubSea Dispersant Injection (SSDI) at the source during three week-long periods representing different atmospheric mixing conditions. Spatially varying time histories of atmospheric VOCs within ~2 km from the release site were estimated. As compared to the no-intervention case, SSDI dispersed the discharged oil over a larger water volume at depth and enhanced VOC dissolution and biodegradation, thereby reducing both the total mass of VOCs released to the atmosphere and the concentration of VOCs within 2 km from the release site. Atmospheric conditions also influenced the VOC concentrations, although to a lesser degree than SSDI.

## 1. Introduction

The atmospheric concentration of volatile organic compounds (VOCs) released during an oil spill has not been extensively studied either by numerical modeling or by collection of data during an event. During the Deepwater Horizon (DWH) oil spill, a wide range of VOCs and secondary organic aerosols derived from the VOCs were measured from an aircraft over oil slicks (Middlebrook et al., 2011; Ryerson et al., 2011; de Gouw et al., 2012; Drozd et al., 2015). In addition to the VOCs evaporating from the oil, the measurements included compounds derived from smoke from in situ burns, combustion products from the flaring of recovered natural gas, and ship emissions from the recovery and cleanup operations (Middlebrook et al., 2011).

It has been suggested that injecting dispersants at the source of a deepwater (subsea dispersant injection, SSDI) blowout can reduce the total mass and concentration of atmospheric volatile organic compounds (VOCs) by dispersing oil in the water column to allow greater dissolution and biodegradation of volatile oil components (Brandvik et al., 2013, 2016, 2017; Brakstad et al., 2015; Socolofsky et al., 2015;

Zhao et al., 2015; Testa et al., 2016; Gros et al., 2017; Daae et al., 2018). In addition, oil that does eventually surface will disperse over a larger area and further from the subsea source. One benefit of SSDI, particularly near the source, is to reduce the potential for well-control responders to be exposed to VOCs. Based on their nearfield model calculations for the DWH spill on 8 June 2010 (representing June 3–July 15) of the deep-water intrusion between 900 and 1300-m depth, Gros et al. (2017) concluded that VOC (defined by the authors as petroleum compounds in the C1–C9 boiling point range) emissions near the wellhead were decreased 28% by subsea dispersant injection.

SSDI is a new oil spill response method that was first deployed to mitigate the effects of an oil-well blowout in during the Deepwater Horizon incident in 2010. Since then, a significant amount of research has been completed to understand how injecting dispersants into a jet of oil released in deepwater modifies the fate of the oil (Brandvik et al., 2013, 2016, 2017; Socolofsky et al., 2015; Zhao et al., 2015; Testa et al., 2016; Gros et al., 2017; Nedwed, 2017; Daae et al., 2018). This and other research has been used to validate near-field blowout and oil spill transport and fate models that predict the volume and location of

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water that will contain oil above a specified concentration, the thicknesses and locations of surface oil, and the amount and locations of oil that could strand on shorelines with and without SSDI application (French-McCay, 2003, 2004; French-McCay and Rowe, 2004; Spaulding et al., 2015, 2017; French-McCay et al., 2015, 2016, 2018a, 2018b, 2018c, 2018d; Li et al., 2017a, 2017b). Further, these models can be used to estimate how application of various oil spill response methods or combinations of methods modify the fate of the oil (e.g., USCG, 2004; French-McCay et al., 2004a, 2004b, 2005, 2018d; Buchholz et al., 2016).

The present study used numerical models to investigate atmospheric VOCs emitted from floating oil and evaluate the effects of SSDI on the total mass and concentration of VOCs for a hypothetical deepwater well blowout in the Gulf of Mexico. The modeling included the following components:

- Near field blowout modeling with OILMAP DEEP (Spaulding et al., 2017; Li et al., 2017a) to determine blowout plume trap height and initial droplet sizes;
- Far-field oil fate modeling in the water column using SIMAP (French-McCay, 2004; French-McCay et al., 2018d) to determine evaporative flux within a delineated study area that changes intensity and location over time;
- Atmospheric modeling using SCICHEM/SCIPUFF (Sykes et al., 1985, 1999 and EPRI, 2017) for six scenarios (three wind conditions, with and without SSDI) using the evaporative flux as input; and
- SCICHEM/SCIPUFF output post processing to determine the spatio-temporal patterns of atmospheric concentrations of VOCs within ~2 km of the release site (the location where well-control vessels will likely be located).

The objective of the study was to evaluate how treatment of oil from a deepwater release with dispersant (SSDI) would affect spatial-temporal patterns of atmospheric VOCs for different environmental conditions and if the subsea injection of dispersants would significantly affect exposure of responders working in the vicinity of the blowout. The focus was on a deepwater blowout, i.e., a situation where an oil and gas buoyant plume would be deep enough to not reach the water surface and where only the oil phase would reach the surface to form oil slicks carrying volatiles that would evaporate. Evaluations of the fate of the gas from the DWH spill (a deepwater spill at a similar depth to the study case example) have shown that the gas was dissolved at depth and did not reach the surface (Valentine et al., 2010; Kessler et al., 2011a, 2011b; Ryerson et al., 2011, 2012). The modeling approach evaluates the surfacing of oil droplets, weathering of the oil in the water column prior to surfacing, evaporation of volatiles from the surfaced oil, and expected atmospheric concentrations above the surfaced oil. VOCs modeled in this study include benzene, toluene, ethylbenzene and xylene (BTEX), C3-benzenes, and C5 to C9 alkanes.

## 2. Methods

### 2.1. Literature search – VOC thresholds of concern

We reviewed occupational standards and interviewed Industrial Hygienists who work on oil spill response to establish the relevant thresholds of concern for a set of VOCs as well as total VOCs. For this study, VOCs included all hydrocarbons with boiling points < 380 °C.

### 2.2. Modeling approach

#### 2.2.1. Modeled scenarios

All modeling was performed at a hypothetical spill location in the northeastern Gulf of Mexico (in De Soto Canyon, Fig. 1). The site does not represent any specific operational site though was chosen from the database of unleased sites with a depth > 1000 m, as was of interest

for the study. The location was 222 km (120 nmiles) from the nearest shoreline (which is Apalachicola on the Florida Panhandle, to the northeast) and about 326–378 km (176–204 nmiles) from the nearest ports where logistics would be based (i.e., 326 km – Passagoula, MS; 330 km – Mobile, AL; 378 km – Port Fourchon, LA). The water depth at the location is 1400 m.

#### 2.2.2. Atmospheric tracer study with SCICHEM/SCIPUFF atmospheric dispersion model

Prior to performing the full oil transport and fate modeling, a tracer study was completed using the SCICHEM model. The SCICHEM model is SCIPUFF (Second-order Closure Integrated Puff) with Chemistry. However, chemical reactions in SCICHEM were not simulated so only the SCIPUFF features were utilized and herein the model is referred to as SCIPUFF. The tracer modeling was performed to identify wind conditions that would produce weak, typical and strong atmospheric dispersion. These wind conditions were used as three wind scenarios for the full modeling. SCIPUFF (Sykes et al., 1985, 1999 and EPRI, 2017) has been previously used for various continental scale tracer studies (e.g., Sykes et al., 1993; Lee et al., 2009). Sage Management is the developer of the SCIPUFF model.

SCIPUFF is a Lagrangian transport and diffusion model that quantifies atmospheric concentrations in three spatial dimensions and over time. SCIPUFF employs a Gaussian puff method (Bass, 1980) to solve the dispersion model equations employing a set of three dimensional puffs used to represent a time-dependent concentration field. The turbulent diffusion parameterization is based on the second-order turbulence closure theories of Donaldson (1973) and Lewellen (1977). SCIPUFF can simulate instantaneous or time varying sources that may originate at single or multiple locations. The source strength and source locations may vary with time.

The tracer study was simulated assuming a stationary source with a strength of 100 g/s released directly above the hypothetical well location. The simulation was run for a period of five years from 2006 through 2010 using time-varying meteorological inputs from the NOAA National Center for Environmental Prediction (NCEP) Climate Forecast System Reanalysis (CFSR) model (NOAA, 2016; Saha et al., 2010). The model predicted surface atmospheric concentrations of an arbitrary constituent. The modeled predictions were post processed to determine the frequency of atmospheric concentrations over an arbitrary reference threshold within 7-day periods. The relative threshold of  $C_{max}/10,000$  was used for this analysis, where  $C_{max}$  was the maximum hourly concentration of the entire set of time series points. The relative threshold was developed on an iterative basis to hone in on a threshold that would provide meaningful results, meaning a threshold that was not so low that a large percent of the area would frequently exceed it nor was it so high that it would rarely trigger an exceedance. The predicted time histories of concentrations within approximately 2 km of the theoretical release location were queried on a grid of 200 m resolution centered on the release location. Then the time histories for all grid cells were processed to determine both the frequency (i.e., percent time) over the relative threshold and an estimate of the area over the relative threshold. The spatial-temporal count of threshold exceedance was summarized for each week-long period and the count for 5th, 50th and 95th percentiles were designated as strong, typical and weak atmospheric dispersion regimes, respectively. An actual 7-day wind data set from the 5-year record was then identified that best matched each condition. These three data sets were used in the full modeling.

#### 2.2.3. Oil spill modeling

##### 2.2.3.1. Oil spill models.

Oil spill trajectory and fate modeling was performed using two sequentially-linked models: OILMAPDEEP (OIL Model Application Package for DEEP water releases; Crowley et al., 2014; Spaulding et al., 2015, 2017) and the SIMAP (Spill Impact Model Application Package) oil fate model (French-McCay, 2003, 2004; French-McCay et al., 2015, 2016, 2018b). OILMAP DEEP evaluates

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