Analysis of How Environmental Conditions Affect Dispersant Performance During Deep Ocean Application

Contracts E14PG00043 and E15PS00027

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Project Support

- This presentation covers work was funded by the U.S. Department of the Interior, Bureau of Safety and Environmental Enforcement (BSEE) through an Interagency Agreement with the U.S. Department of Energy, Pacific Northwest National Laboratory. The work was performed under BSEE Contracts:
  - E14PG00043, “Biodegradation and Toxicity Following Dispersant Usage in a Cold, Stratified, Deep Sea Setting,” and
  - E15PS00027, “Analysis of How Environmental Conditions Affect Dispersant Performance During Deep Ocean Application,”

Project Overview

This study entailed the design and execution of basic and applied research to

1) Better understand the behavior of oil, dispersants, and microorganisms under relevant conditions
2) Identify tools for conducting high-pressure oil research
3) Apply the data and insights to improve how models, such as the Blowout and Spill Occurrence Model (BLOSOM) predict the movement of oil in the marine environment.

Organization of the Presentation and Final Report

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- Background and motivation
- Study methods
- Research tasks, experimental design, outcomes
  1. Characterize the physical state of oil after treatment with a dispersant in a cold, deep, low turbulence setting.
  2. Examine the influence of droplet size on biodegradation.
  3. Explore novel, noninvasive approaches to characterize emulsions and oil degradation in pressure chambers.
  4. Examine the effect of deep water conditions on cell growth and the biodegradation of high concentrations of oil.
  5. Oil and Dispersant Physical Characteristics: Rheometry.
  6. Characterize the effect of pressure drop and temperature on oil droplet size.
  7. Explore the effect of sediments on droplet size.
  8. Update BLOSOM (Blowout and Spill Occurrence Model) to incorporate dispersant effects on droplet size distributions.
- Conclusions and next steps

Motivation

- Oil production in waters of the U.S. Outer Continental Shelf is likely to increase in the foreseeable future.
- According to US Energy Information Administration reporting (4/2017)*
  - There were 8 new field starts in 2016 in waters from 3700 ft to 9556 ft deep
  - For 2017-2018, there are 7 anticipated starts in water deeper than 1200 ft

- Deep ocean exploration represents an important resource to meet growing demands, but the Deepwater Horizon incident of 2010 highlighted a number of uncertainties about spill remediation, and in particular the interplay of oil leaks, dispersants, and biodegradation in the cold and high-pressure environment of the Outer Continental Shelf

*https://www.eia.gov/todayinenergy/detail.php?id=30752

Background

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- Oil breaks down due to physical, chemical, and biological (metabolic) effects, and these are much better characterized for surface conditions

- Dispersants are most effective when used on freshly ejected, non-weathered oil, which is one motivation for applying dispersants at the source of a leak
  - However- there is a need to better understand the process of dispersant-oil-seawater mixing and how and to what degree particular factors (e.g., pressure drop, temperature, sediment, viscosity) affect mixing and ultimately, oil droplet size

Research PNNL Team

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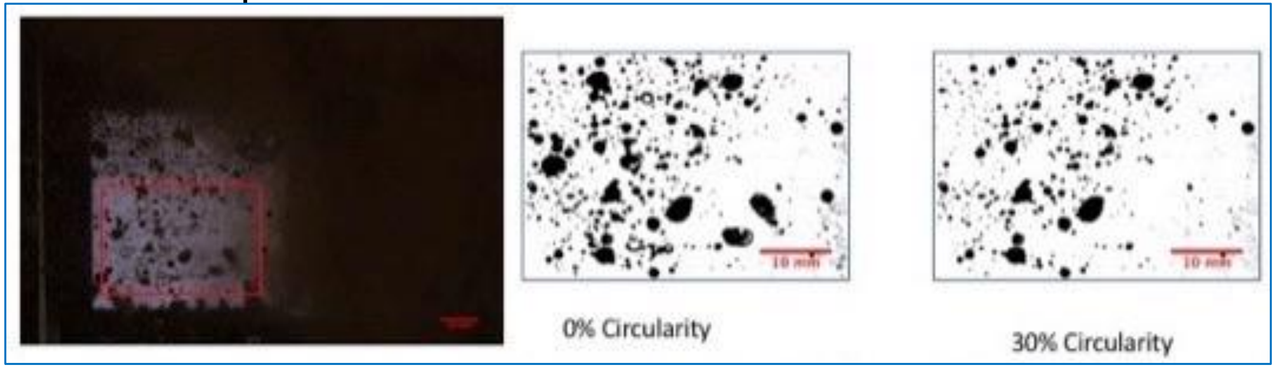
General Study Methods

- Request to use Macondo oil for primary tests
- Request to use high concentrations of oil
- Seawater from Sequim Bay, average salinity of 30.6 ± 0.8 psu
- Droplet size distribution (DSD) determination
  - Challenge with Sequoia devices (LISST-100 and LISST HOLO)
    - Poor imaging in cuvettes with moving oil and with high oil concentrations
  - Use of photography and image processing software
    - Provided wider dynamic range than with the LISST devices and greater flexibility
    - Image processing with Fiji software to identify and size droplets
    - Calibration with plastic bead size standards



Example of particle (droplet) identification in a challenging blowout test image with larger droplets (left side of original) and a large cloud of atomized droplets (right side of original)

1) Characterize the physical state of oil after treatment with a dispersant in a cold, deep, low turbulence setting

- Oil droplet size is considered as an important factor controlling biodegradation - the primary objective for using dispersants is to distribute oil as small, easily degraded droplets in the water column

Key Objective

- Characterize the physical state of oil as a consequence of dispersant action in deep water settings to establish the context within which to characterize phenomena such as biodegradation.
  - Interfacial tension measurements at different temperatures and DOR
  - DSD observations at different pressures and DOR

Interfacial Tension

- Without external mixing forces, two immiscible fluids separate to minimize the surface area between them
  - The smallest possible surface area exists when the fluids are separated as two phases, i.e., all oil in one large drop or slick ; dispersants reduce tension
- Measured using an inverted pendant drop phase method and a ramé-hart 590-U1 Advanced Automated Goniometer/Tensiometer

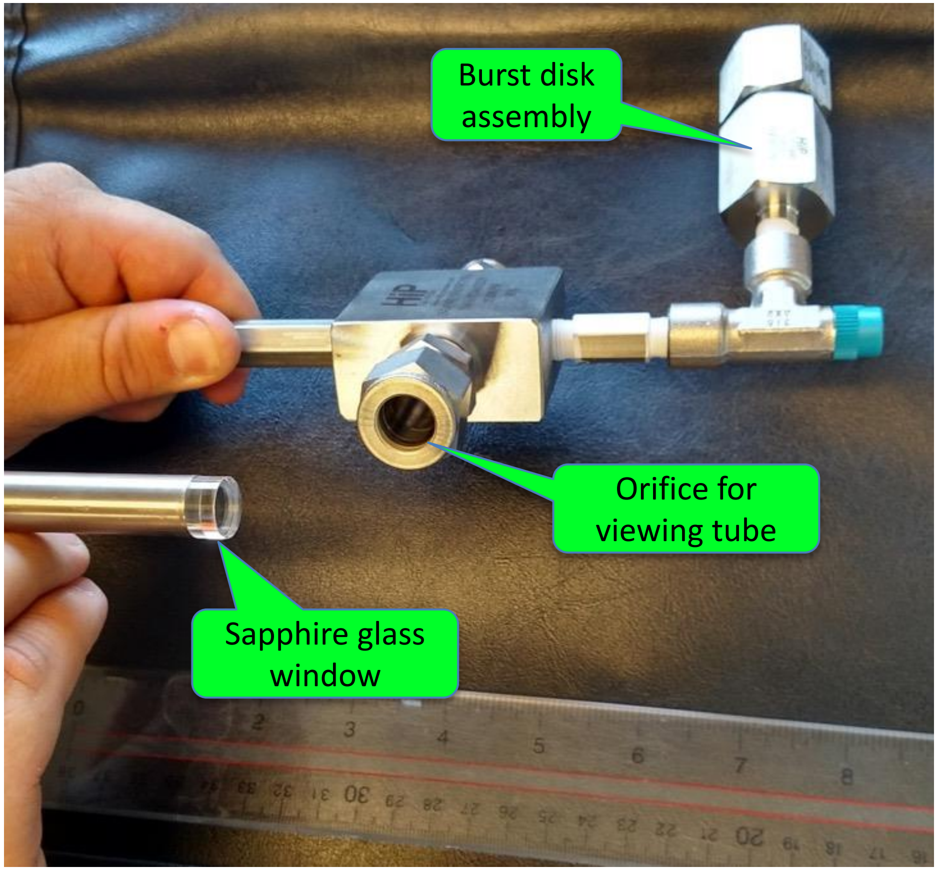
- Interfacial tension was found to increase slightly as the temperature <u>difference</u> between the oil and the water increased
- A somewhat greater effect was observed with the Corexit
- The temperature-induced increase was not proportional to changes in DOR and might therefore be attributed to the oil
- The effect of mismatched and matched dispersant and oil temperatures during mixing in a simulated blowout was explored more carefully under Tasks 5 and 6

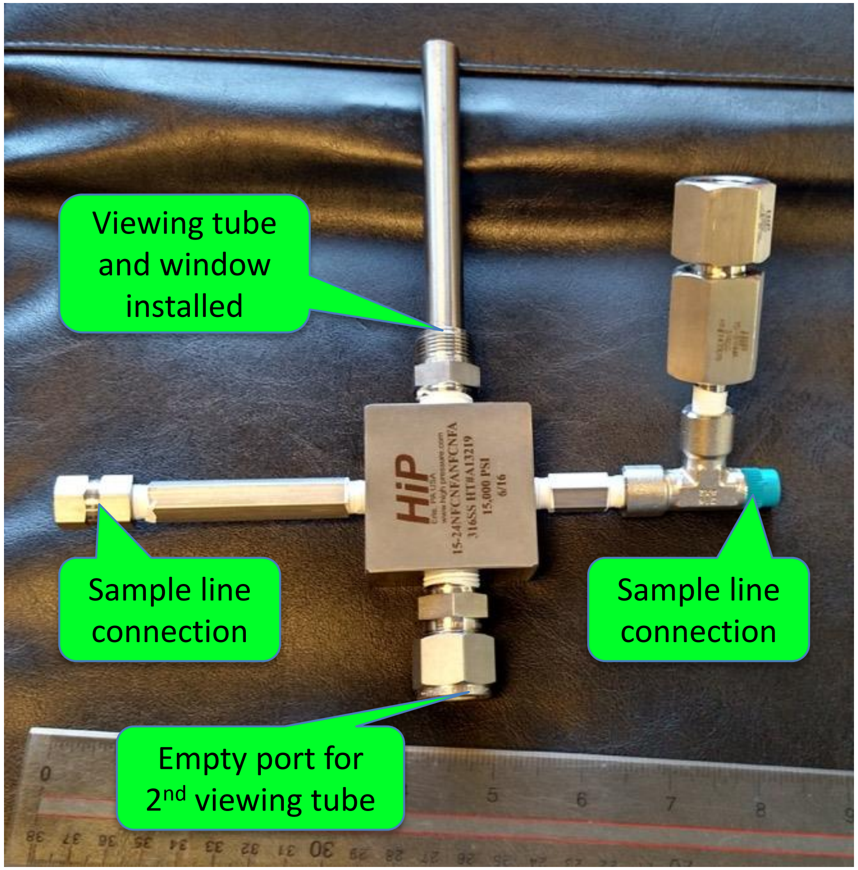
Pressure Systems

- Parr reactors rated to 3000 psi (equivalent to ~2000 m depth)
  - Six, 2-liter reactors made of 2205 duplex and Hastelloy C stainless steel
  - Sample tubes at 3-depths (top, middle bottom)
  - Four mixing units, two static units
  - External chilling to ~5^{o}C (middle image)

High Pressure View Cells

- Provides a 2.4 cm^3 viewing area
- Sample lines connected to Parr reactors or 7500 psi syringe pumps





Resulting Challenges Identified a Need for a Different Approach

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- Oil in the Parr reactors quickly rose to the surface in the absence of mixing energy; mixing alters the droplet size distribution
- Despite testing several oleophobic coatings, none were highly effective with crude oil
- Reducing the amount of oil resulted in no droplets being visible
- Attempts made to rotate (tumble) the small view cells failed to keep droplets in view
- Decision to simulate the effects of an oil blowout and relative changes in pressure, temperature, and GOR

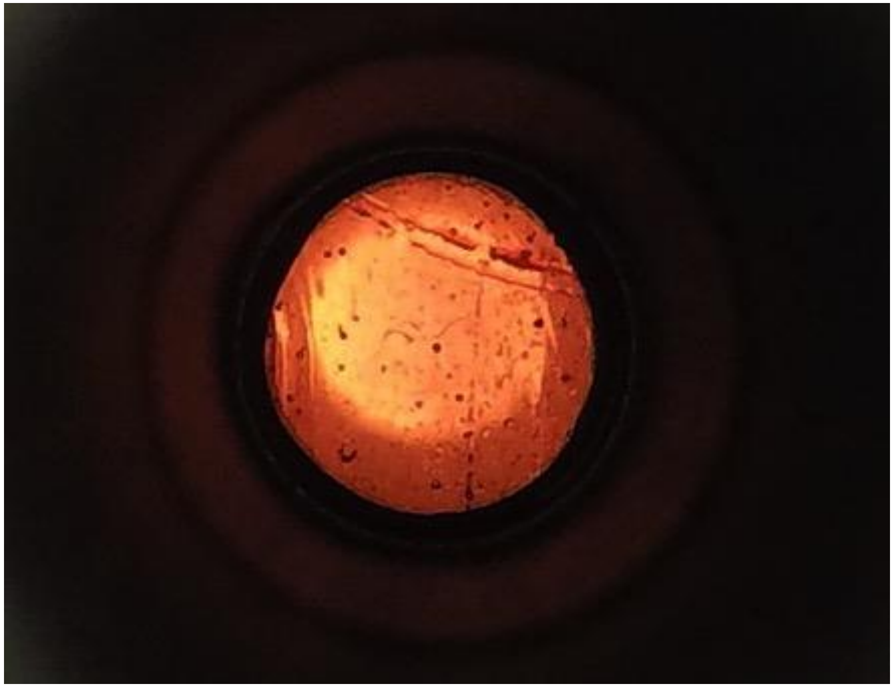

Image taken of 400 µL oil with 16 µL Corexit in 200 mL seawater at 17.8°C. In this image, the view cell window has become coated with oil

2) Examine the Influence of Droplet Size on Biodegradation

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Key Question:

- The influence of droplet size on biodegradation has not been quantified: i.e., we don't know if a 50% decrease in size results in a 50%, 25%, or negligible increase in the rate of biodegradation
- Understanding this has ramifications on how much dispersant to use

Experiment:

- Different methods tested for creating and maintaining droplet sizes
  - None were 100% effective
- Decision to use different concentrations of Corexit with uniform mixing speeds to establish droplet size distribution
  - Used defined cultures of oil-degrading bacteria or mycelial fungi
    - Used defined cultures to eliminate variability from mixed communities
    - Bacteria = droplet surface acting; mycelial fungi = droplet penetrating

Results and Conclusions from the Droplet Size-Biodegradation Experiments

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- Gas chromatography-mass spectrometry (GC-MS) used to quantify and monitor the degradation of alkanes and polycyclic aromatic hydrocarbons (PAH)

- The dispersant did not have any significant negative effects on oil degradation by the species tested
  - Microtox assays found that Corexit was beneficial to the cells

- Droplet size did not have a recognizable effect on either the bacteria or the fungi
  - “Droplet size” is actually a distribution; it may be that the overlap between distributions masks any influence that size has
  - The distributions were not constant
  - It may be that it is simply important to have droplets rather than a slick

3) Explore Novel, Noninvasive Approaches to Characterizing Emulsions and Oil Degradation in Pressure Chambers

Challenge

- Withdrawing samples from a pressure system may result in alteration of the sample (e.g., by degassing, shear forces)
- Methods such as GC-MS and solvent extraction spectroscopy are time consuming and expensive

Objective

- Test a variety of non-invasive methods to characterize DSD, DOR, and oil chemistry (i.e., detect biodegradation)

Methods examined

- Nuclear magnetic resonance spectroscopy (NMR)
- Fluorescence spectroscopy – particularly high throughput devices
- Hyperspectral imaging

Results and Conclusions

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- NMR could be effective, but the challenge is the ability to hold oil droplets steady
  - High resolution requires several minutes
  - Oil smears on sidewalls may not be a problem

- Light imaging methods are all sensitive to oil smears
- Hyperspectral imaging might work for very low concentrations of oil (<0.1%), but this was below our test parameters
  - Hyperspectral imaging appeared to be effective for measuring dispersant
  - Oil droplets might be visible through negative imaging (hole in the water)
- Oil concentrations >1% interfered with fluorescence spectroscopy
- Acoustic methods: velocity attenuation and backscatter were not tested, but should be effective for monitoring chemical changes and perhaps DSD

4) Examine the Effect of Deep Water Conditions on Cell Growth and the Biodegradation of High Concentrations of Oil

- A significant portion of the oil from the Deepwater Horizon blowout settled on the seafloor
- Our modeling work demonstrates that dispersant use can send some oil to the seafloor
- Surface microorganisms naturally enter deep ocean (>1000m) microbial communities and may be able to enhance biodegradation

Questions

- How do deep ocean conditions impact biodegradation by surface organisms?
- What is the relative impact of pressure versus temperature on biodegradation?

Findings and Results

Literature Review

- Influence of depth:
  - Light is negligible below 300m (even shallower in many areas)
  - Mixing zone, the upper ~200m, shows little change in temperature from surface, but temperatures drop quickly below 200m
    - Temperatures below 1000m are typically steady $\leq 4^{o}C$
- Limited research available on hyperbaric microbiology and less still on the effect of pressure on oil degradation (some recent papers)
- Pressures representing depths up to 1000m (~1470 psi) have little effect on biodegradation, but some species are affected as pressures increase above 1500 psi
- Enzyme complexes may be more susceptible to pressure than monomers

Experiments and Results

- Collected and concentrated mixed microbial community from 252 liters of seawater
  - Created and cryopreserved a set of small 50x concentration aliquots to use in experiments and to maintain consistency
  - Colleagues at MBARI, WHOI, and elsewhere could not provide significant volumes from deep ocean collections
- Request was to use ≥1% oil in seawater (vol:vol)
  - **Most biodegradation studies use 0.00025% to .0015%**
  - 1% was too high however- signatures of biodegradation were masked by the undegraded oil
- Monitored growth curves of cells grown on mixed carbon sources
  - Determined that reduced temperature had a greater effect on cell metabolism than pressure

5) Oil and Dispersant Physical Characteristics: Rheometry

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- A number of factors influence droplet size and the potential for coalescence; among these are the viscosity and density of the fluids, surfactant concentration, dilution of the oil in water, and interfacial shear

Question

- Does matching the temperature and density of the dispersant with the ejected oil have any effect on the extent of oil and dispersant mixing and thus the emulsification of the oil?

- In preparation for empirical testing, experiments were conducted to obtain high-quality density and viscosity data for the oil (Macondo and ANS) and dispersant (Corexit and Finasol) samples as a function of temperature

Results and Findings

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- Data (graphical representations of viscosity and density relative to temperature) for the samples is provided in the report
- Density could not be obtained for the Macondo oil at 70°C as there was too much degassing
- Dynamic (absolute) viscosity from 4°C to 100°C at a shear rate of 100/s was obtained for all four samples
  - These materials are non-Newtonian and thus instead of exhibiting a consistent dynamic viscosity no matter what the applied shear force, these materials exhibited shear-thinning behavior
  - In a blowout setting, oil near the orifice would have a lower viscosity than predicted merely from temperature; dispersant ejected at a high rate from a small orifice, or into an oil ejection plume will also have a lower viscosity
  - Continued turbulence from degassing could also reduce the viscosity of the oil and dispersant in an ejection plume

6) Characterize the Effect of Pressure Drop and Temperature on Oil Droplet Size

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- A number of factors experienced by oil ejected during a blowout, such as pressure drop, degassing, and temperature drop may impact how an oil, dispersant, and seawater mix to form an emulsion
- The means by which a dispersant is injected into the oil plume, including how its temperature or viscosity match that of the oil, may also affect mixing

Questions:

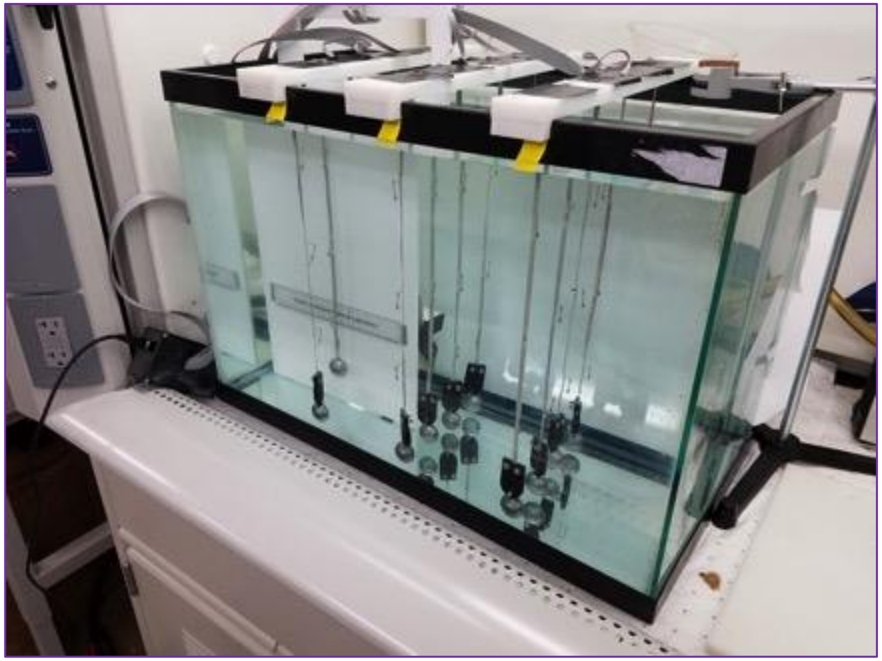
- How do factors such as degassing, temperature drop, and pressure drop affect droplet size distributions?
- How does the temperature of the dispersant affect mixing and DOR?

Experimental Setup

- Oil was pressurized in the 2-Liter Parr reactors (~2900 psi)
  - Gas injected into headspace to pressurize (resulting in a lower GOR)
  - Gas injected into the oil (resulting in a higher GOR)
  - The Parr reactor was heated or left at room temperature
- A volume of pressurized oil was released into a tank to simulate a pressure drop
- Dispersant was premixed with the oil, co-injected, or not added

Test tank showing the 4×3 thermal probe array. Each wire had three thermistors along its length to interrogate the top, middle, and bottom depths of the tank.

A white polypropylene sheet provided a backdrop and defined field of view for photographing oil droplets.



Videography and Photography

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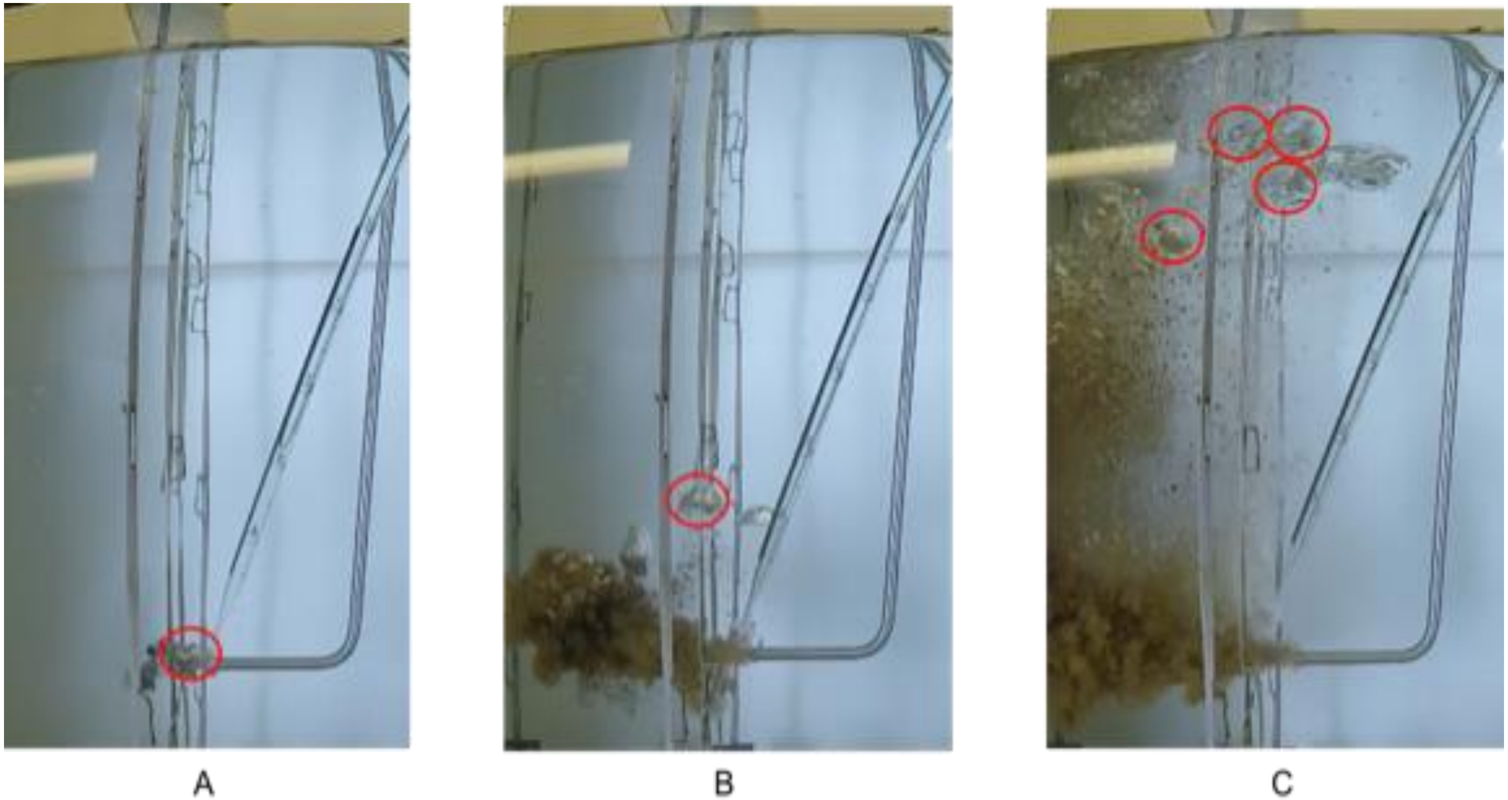
- The camera system was computer controlled to collect images over a 10 minute period
- A ruler in the camera field of view provided a calibration standard

Gas Emission Can Separate the Dispersant from the Plume



Time series of images during a Macondo crude oil blowout (43 grams released at 60°C and 2400 psi) with coinjection of 1.0 g of Corexit EC9500 (17.4°C and 1 atm) into raw seawater (11.8°C and 1 atm).

Test Parameters

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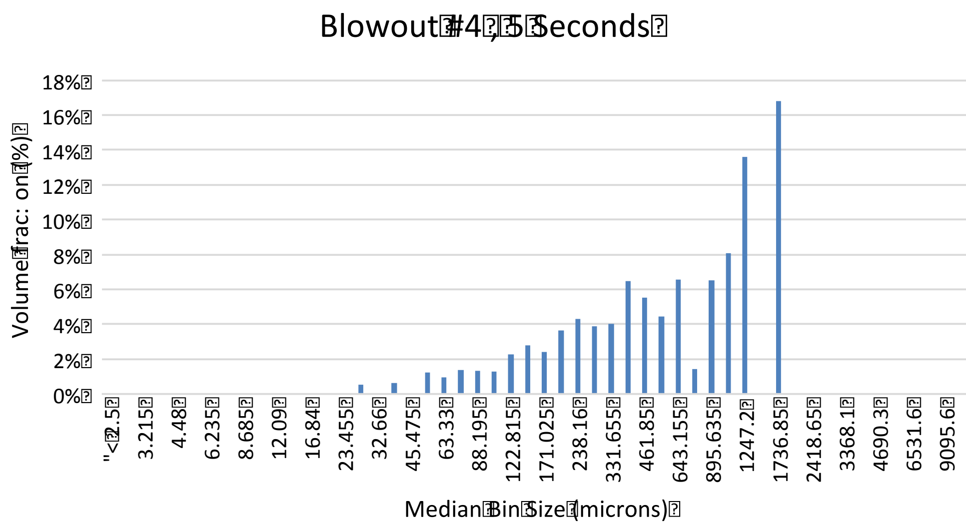
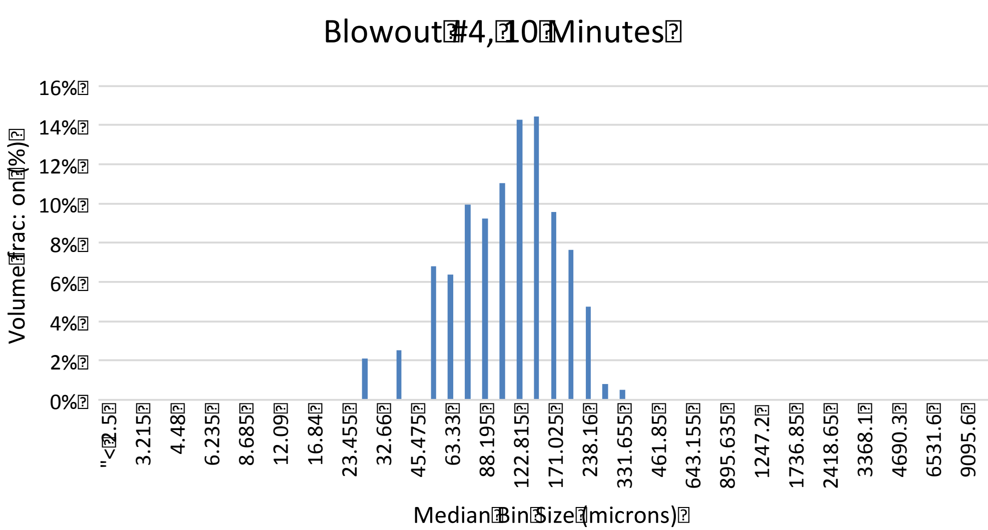
- Seawater was always chilled (started at 4^{o}C)
- Oil was either heated (60^{o}C or at 16.8^{o}C)
- Dispersant (if used) was either at 4^{o}C, 16.8^{o}C, or 60^{o}C)
- Dispersant was either premixed with the oil (perfect mixing) or co-injected near the oil tube orifice
- The weight of seawater, oil, gas, and dispersant used was always determined

- Droplet size distributions were determined ~5 seconds into the blowout (using multiple photographs) and at 10 minutes following the blowout

Example of Blowout Data





Seawater	4°C
Oil	60°C
Dispersant	none
Injection Style	N/A
Pressurization	Headspace
Starting Pressure	2345
Ending Pressure	1775
Drop	570
Dispersant	0
Oil+Gas released	151 g
Oil Released	151 g
DOR	N/A
Seawater	64020.5

Results

- In all blowout tests, a cloud of atomized oil droplets <10 µm (with many droplets <1 µm) was created and lingered for >10 minutes in the tank
  - Rapid degassing and the shear forces from the ejection cause significant atomization, but the cloud of droplets represents a small mass fraction of the oil
- In the absence of dispersant, the cloud eventually formed a gravity-based gradient with some clearing at the bottom of the tank and increased density of particles (opaque appearance) at the top of the tank
- In the presence of dispersant (co-injected or premixed), the surface slick was discontinuous
- There was no significant difference in droplet size distributions when the dispersant was premixed or co-injected with the oil

7) Explore the Effect of Sediments on Droplet Size

- Organic and inorganic particles found in crude oil and the water column may have an impact on droplet size during a blowout
- The formation of stable oil-particle-aggregates (OPAs) in coastal environments following a spill is well-documented, though typically associated with weathered oil
  - An important factor in the formation of these aggregates along the shoreline is turbulence, and the turbulent discharge of oil from a leaking well might promote the formation of aggregates

Question

- Does the presence of sediment impact DSD with or without the presence of a dispersant?

OPAs

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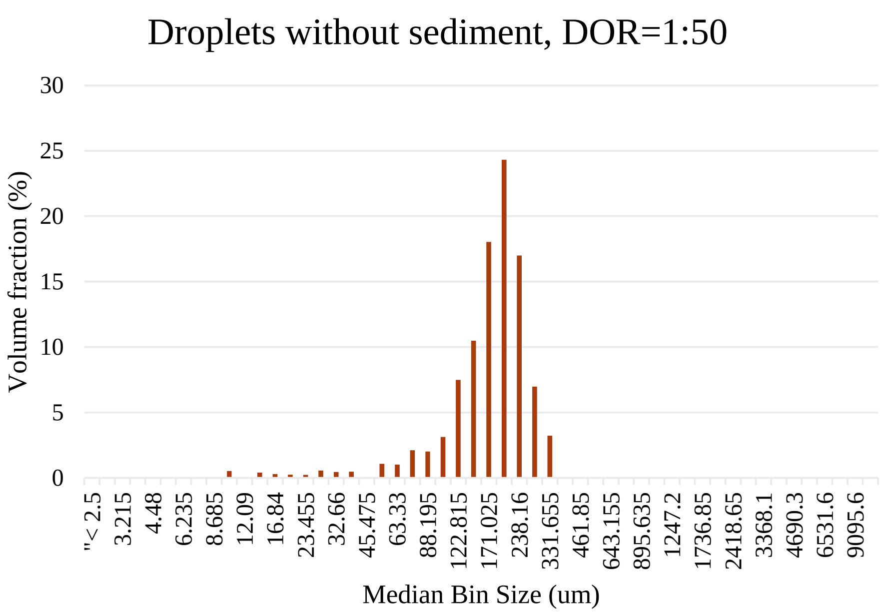
- The potential formation of OPAs during a deep ocean release would have important ramifications for the fate and transport of the oil
- OPAs have a lower interfacial tension with water than does oil alone, and are thus less likely to coalesce
- OPAs also tend to have a higher specific gravity and to sink in water
- OPAs may form with a wide range of sediment and mineral types, or with phytoplankton
- OPAs will form when the concentration of sediment is as low as 100 mg sediment per liter of seawater

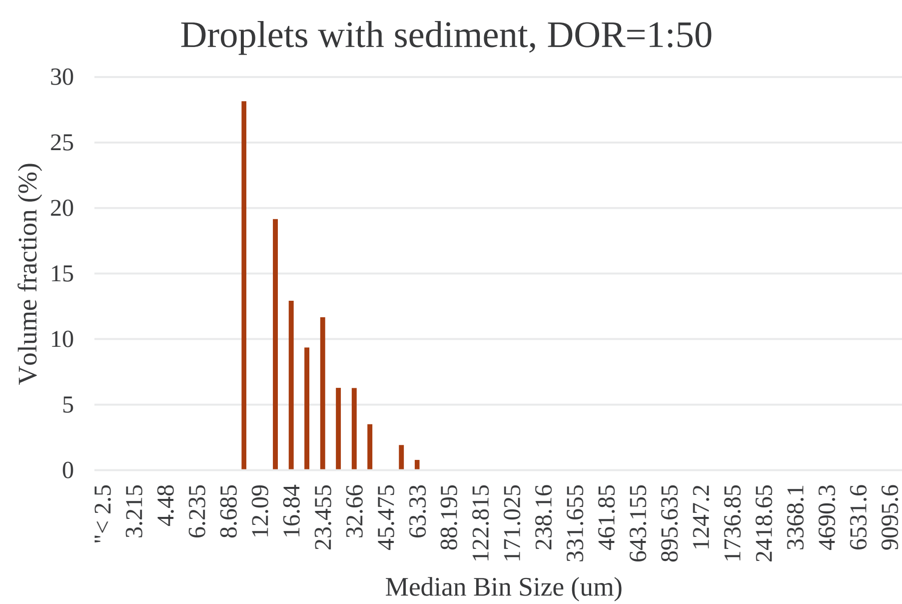
Experimental Design

- 200 µL of oil with and without 50 mg of fine sediment (diatomaceous earth) was added to 200 mL of seawater (1:1000 oil to water ratio) in 500 mL glass beakers, and mixing energy was provided by a magnetic stir bar at 240 rpm
- Mixing energy was stopped to allow for photography (within a few seconds of stopping) and particle size determination
  - Photos of the water surface and potential oil slick formation were taken after 2–3 min without mixing
- Mixing was restored and then 4 µL of Corexit 9500 was added to each beaker to achieve a DOR of 1:50
  - Mixing continued for 5 min at which point a second set of photographs were taken
- Mixing was again restored and an additional 4 µL of Corexit was added to achieve a DOR of 1:25
- A control flask with the sediment remained turbid when mixing ceased

Results and Conclusions

- Prior to the addition of the dispersant, samples with and without sediment had a fairly similar droplet size distribution in the smaller bin sizes, but the sample with no sediment had larger droplets representing a significant fraction of the total volume
- With the addition of Corexit at a DOR of 1:50, however, the samples with sediment had a distinctly lower size distribution (maximum diameter of 62 µm), while the sample without sediment had droplets with a maximum diameter of 359 µm





Subsea Dispersant Modeling Task Using BLOSOM

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Modeling Goals:

The response community would benefit from the following:

- To reflect recent results from the large volume experimental studies of subsea dispersants released via publications.
  - These offered opportunity to derive new relationships to incorporate into models to improve simulations
- BLOSOM's dispersant module leveraged multiple droplet models including:
  - Johansen et al., 2013
  - PNNL Experimentally derived from results of tasks 1-4.

Modeling Objectives:

- Implement and validate Johansen et al. 2013 droplet size distribution from literature.
- Compare simulations using Johansen et al. 2013 distributions to PNNL results both with and without dispersant treatment.
- Capture new dynamic relationship extracted from the literature.

Desired Outcomes:

By improving dispersant application modeling, predictive qualities of BLOSOM increase.

- Improved simulation for theoretical, "what if" scenarios.
- Ability to simulate more scenarios to assist response planning & actions
- Improved realism of oil's fate after application

NETL Team

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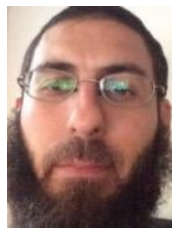
Ward Burgess



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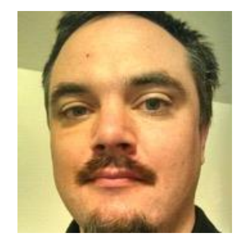


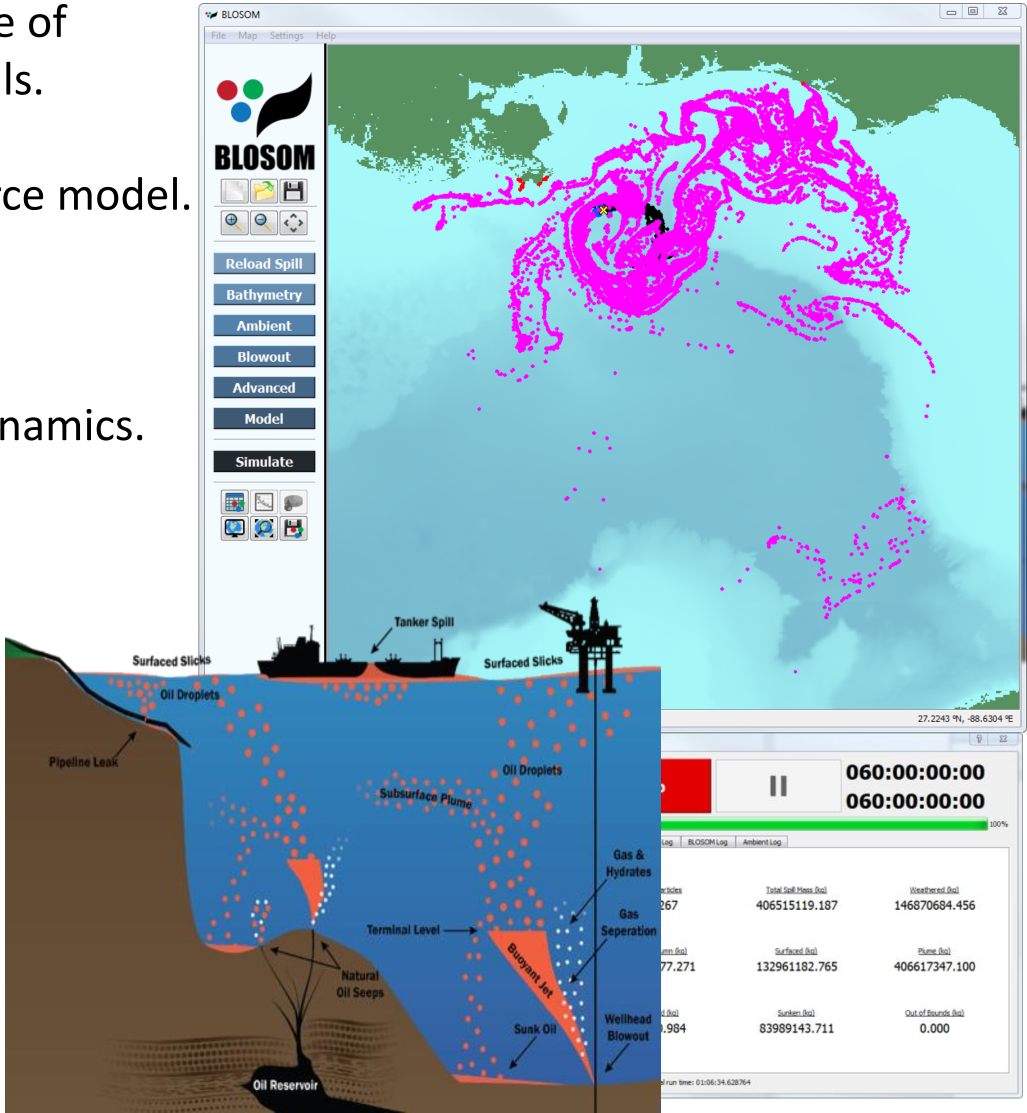
Patrick Wingo

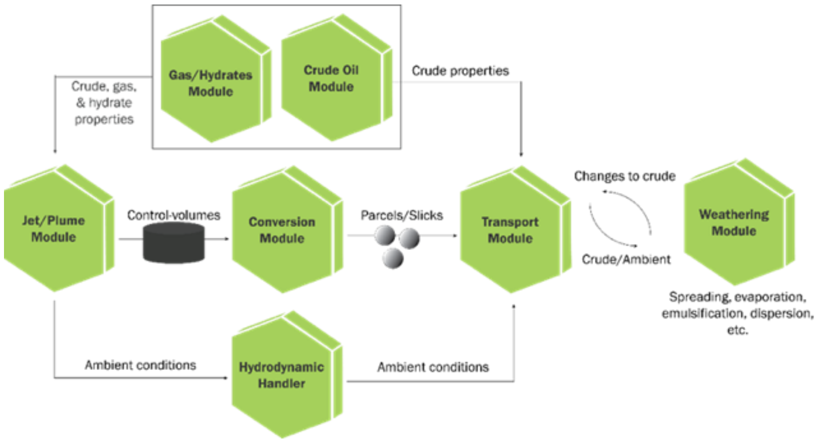
What is BLOSOM?

- The Blowout and Spill Occurrence Model (BLOSOM) is a 4D fate and transport model capable of simulating deepwater blowouts and spills.

- Developed by the NETL as an open-source model.

- Current simulation captures:
  - Jet/Plume behavior
  - High pressures, gas and hydrate dynamics.
  - Multiple Droplet Size Distributions.
  - Subsurface Plume formation.

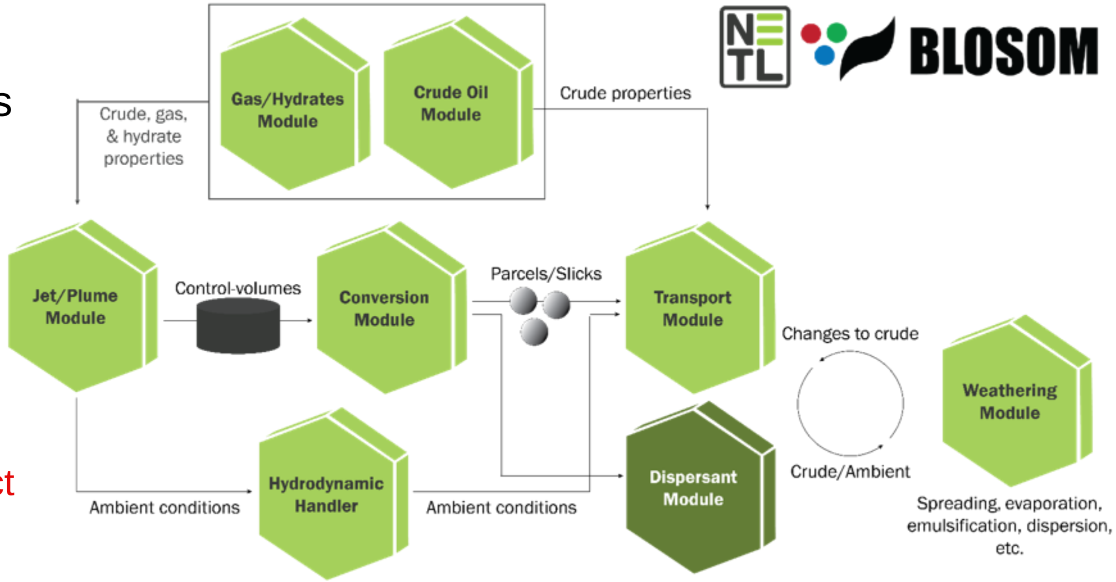




What was Completed: Subsea Dispersant Modeling in BLOSOM

A new Dispersant module was constructed for BLOSOM.

- Developed a module to model dispersant treatment effectiveness as a factor of oil viscosity.
- Module incorporated several droplet models for simulation
- Johansen et al. 2013.
  - PNNL 2017 untreated. ←This project
  - PNNL 2017 treated. ←This project
- Initiated ability for user to define where dispersant application will occur.
  - Preliminary code in development that will allow user to pick where in the plume/spill the dispersant is being applied.
  - Foundation for future work.



What does the Subsea Dispersant Module Do?

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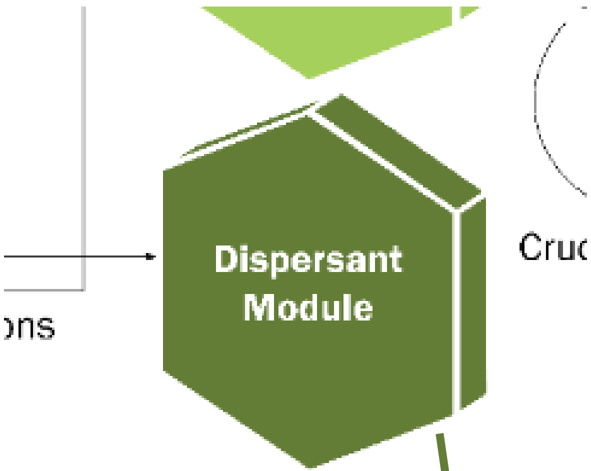

- Defines and utilizes relationship between viscosity and Dispersant Efficiency.
  - Uses the current crude viscosity calculated from Mackay et al 1982.
- Defines several droplet size distributions used to represent both treated and untreated oil.
  - Johansen et al. 2003.
  - Johansen et al. 2013.
  - PNNL distributions.
- Defines Preliminary Groundwork for future efforts.
  - Selection of specific regions, times for dispersant application.

How Subsea Dispersant Module was Constructed: Dispersant Effectiveness/Viscosity Relationship

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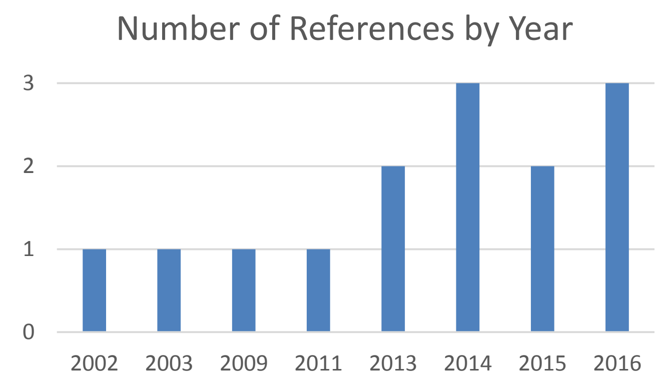
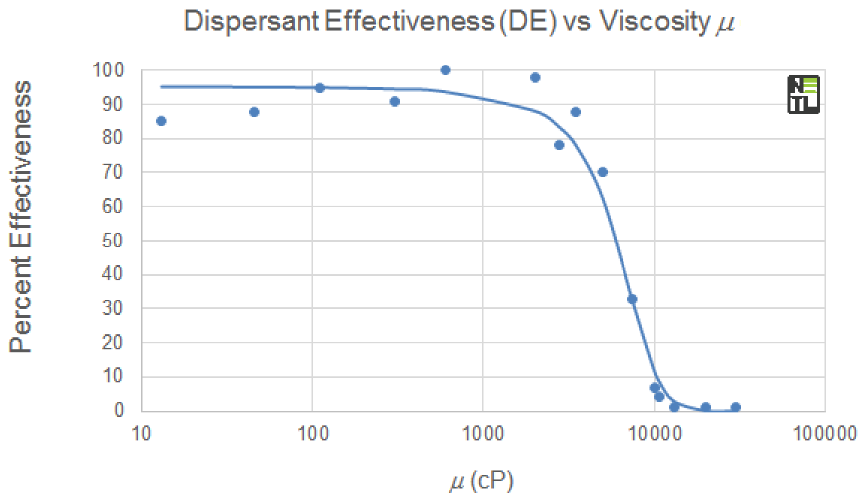
Step 1 - Literature Review: 35+ articles collected.

- Dispersant Effectiveness / viscosity relationships were extracted from 14 studies.
  - Ranging from 2002-2016*



Key Highlights Identified From This Review:

- As viscosity increases, the effectiveness of dispersant treatment decreases.*
  - Significant drop between 1000 and 10000 centipoise (cP).
- Two protocols used to measure dispersants effectiveness; both are selectable in BLOSOM.
  - Institut Français du Pétrole (IFP) – France. (Guyomarch et al., 2016)
  - Mackay-Nadau-Steelman (MNS) – Norway. (Guyomarch et al., 2016)



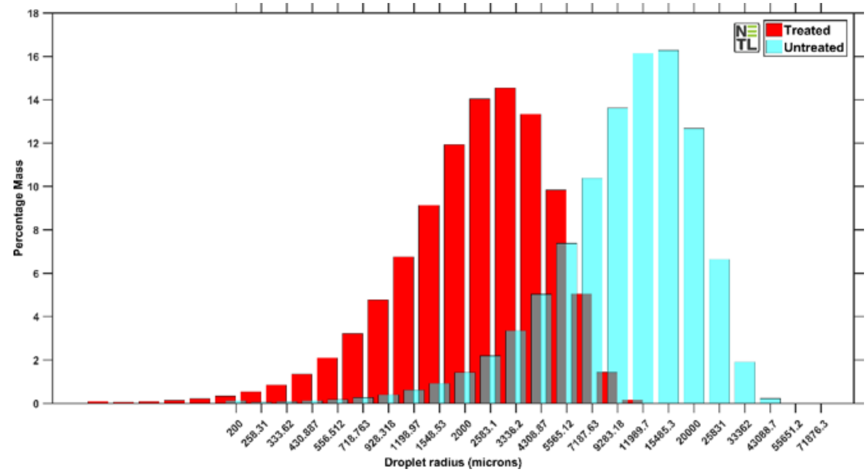
* Moles et al., 2002; Chandrasekhar and Sorial, 2003; Belore et al., 2009; Mukherjee et al., 2011; Wang et al., 2013; Brandvik et al., 2013; Abdelrahim and Rao, 2014; Nagamine, 2014; Fu et al, 2014; Nyankson, 2015; Nyankson et al., 2015; Brandvik et al., 2016; Pan et al., 2016; Zhao et al., 2016

By integrating this relationship into BLOSOM, we can estimate the efficiency of dispersant application based on an oil's viscosity.

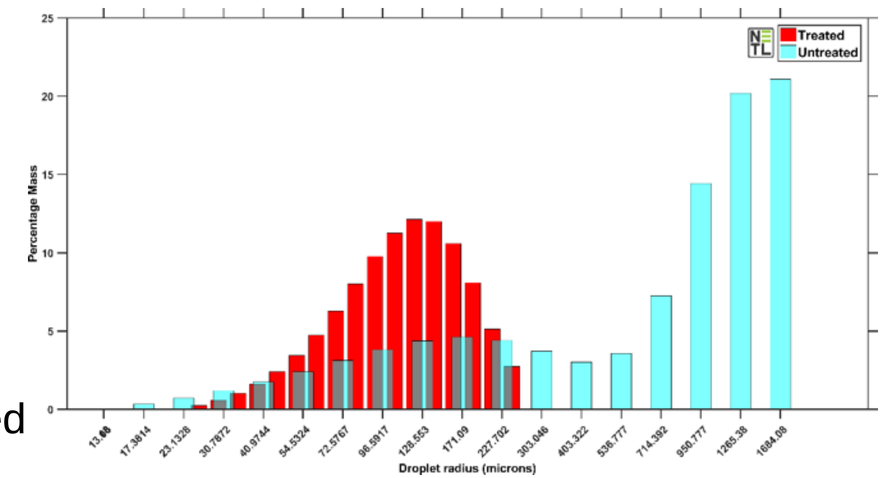
How Dispersant Module was Constructed: Droplet Size Distributions from BLOSOM

Integration of droplet size models into custom BLOSOM Module:

- Application of dispersants reduces the median and range of oil droplet sizes.
- Sanity check: Droplet Size distribution generated by BLOSOM matches Johansen et al. 2013 when option is selected.
  - Both treated and untreated distributions unimodal.
- PNNL experimental distributions are off by about a magnitude when compared to Johansen et al. 2013.
  - Treated distribution unimodal, untreated distribution bimodal.
- Based on differences in distributions, simulated results should come out differently.



Johansen et al. 2013



PNNL Experimental Results

Validation: Realistic Gulf of Mexico Simulations

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- Realistic 3D+time simulation of ocean ambient conditions from NCOM (Navy Coastal Ocean Model) including ocean currents, temperature, salinity.
- Simulation initiated from Macondo well on May 20, 2010 and run for 60 days with PNNL2017 and J2013 DSDs **treated** and **untreated** blowouts (~1500m depth).

	0-250m	250-500m	500-750m	750-1000m	1000-1250m	<-1250m
J2013 T	42.1	0.6	0.9	1.3	2.2	52.9
J2013 NT	87.1	0.6	0.7	0.8	1	9.9
PNNL T	2.7	0	0	0	0	97.3
PNNL NT	3.8	0.3	0.3	0.6	1.8	93

It is important to simulate the use of dispersants, otherwise the oil distribution observed in a real-life blowout where dispersant was used, would be missed by a big margin. The 50% of oil remaining at depth is consistent with observations from the deepwater Horizon.

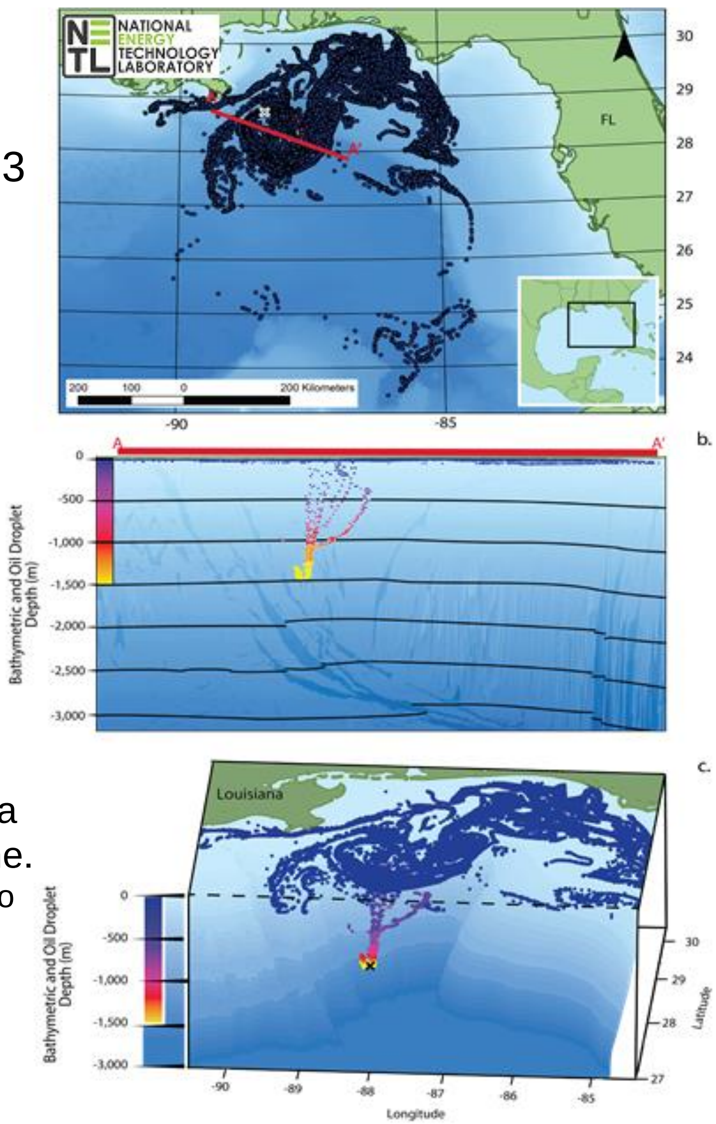
Simulations with DSDs from Johansen et al., 2013

Validation with Johansen et al. 2013 simulation results.

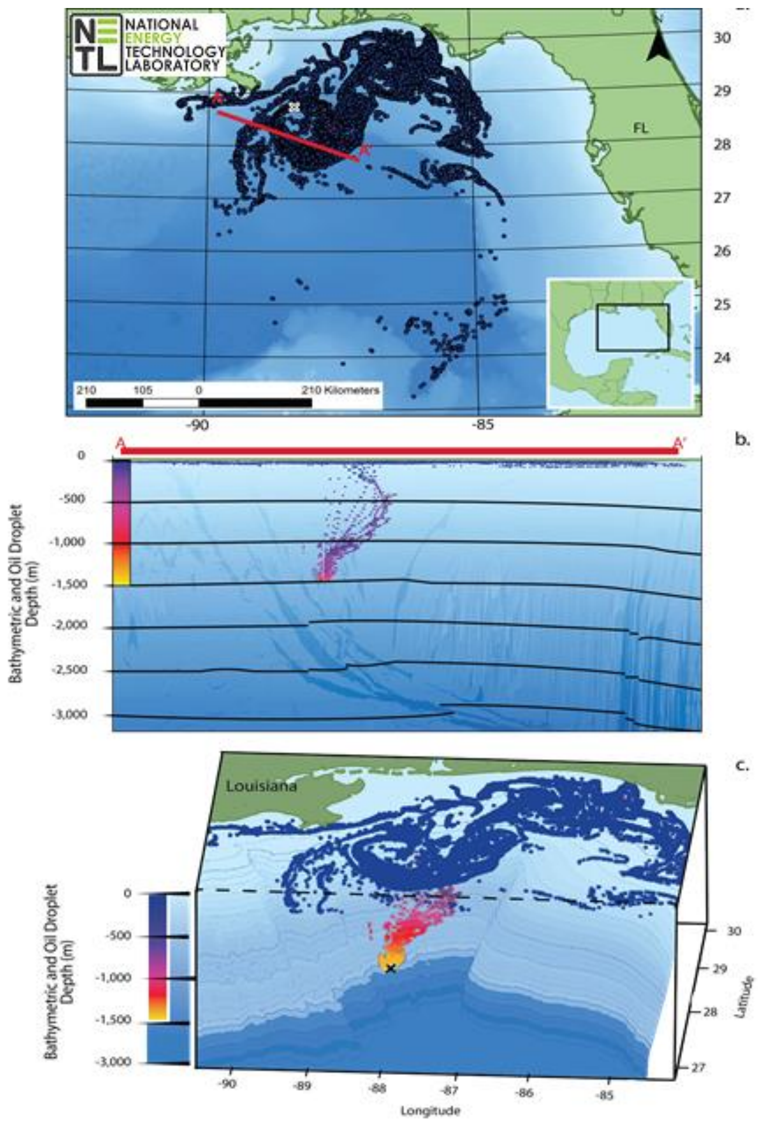
Less oil made it to the surface when treated with dispersant

Treated oil resulted in a wider subsurface plume.

- Smaller droplets cease to rise and spread out horizontally.
- This is the expected behavior.



Untreated



Treated

Simulations with DSDs from PNNL Experiments

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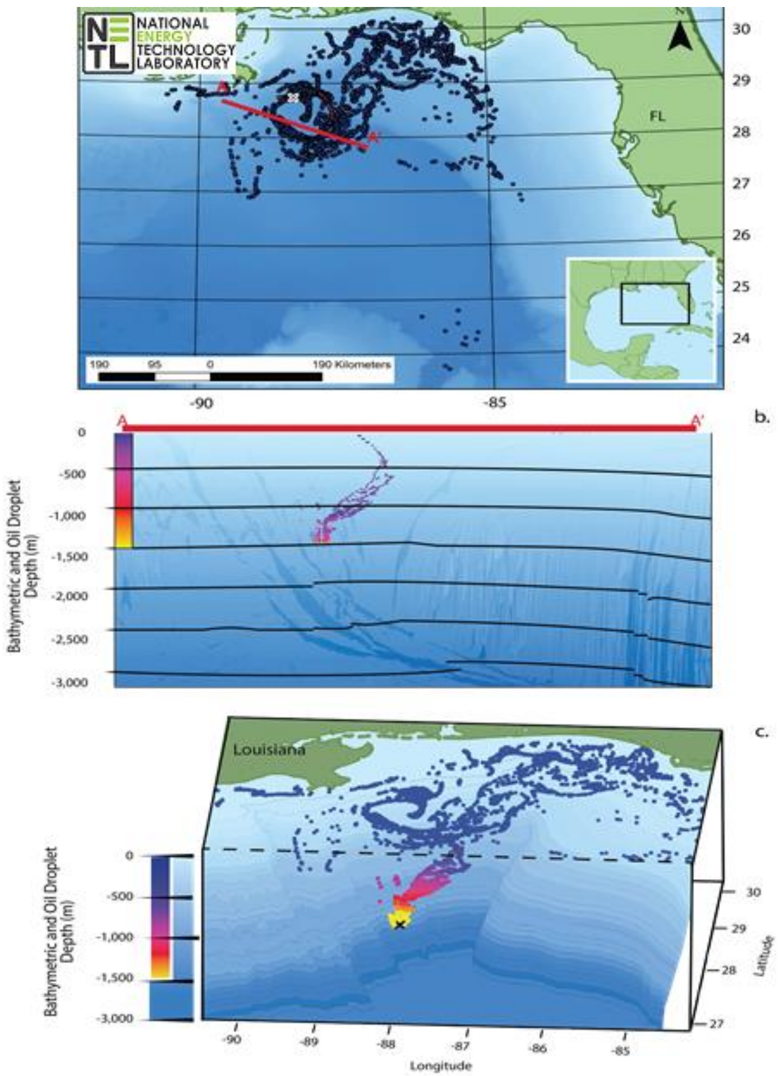
Simulation with PNNL Experimental simulation results.

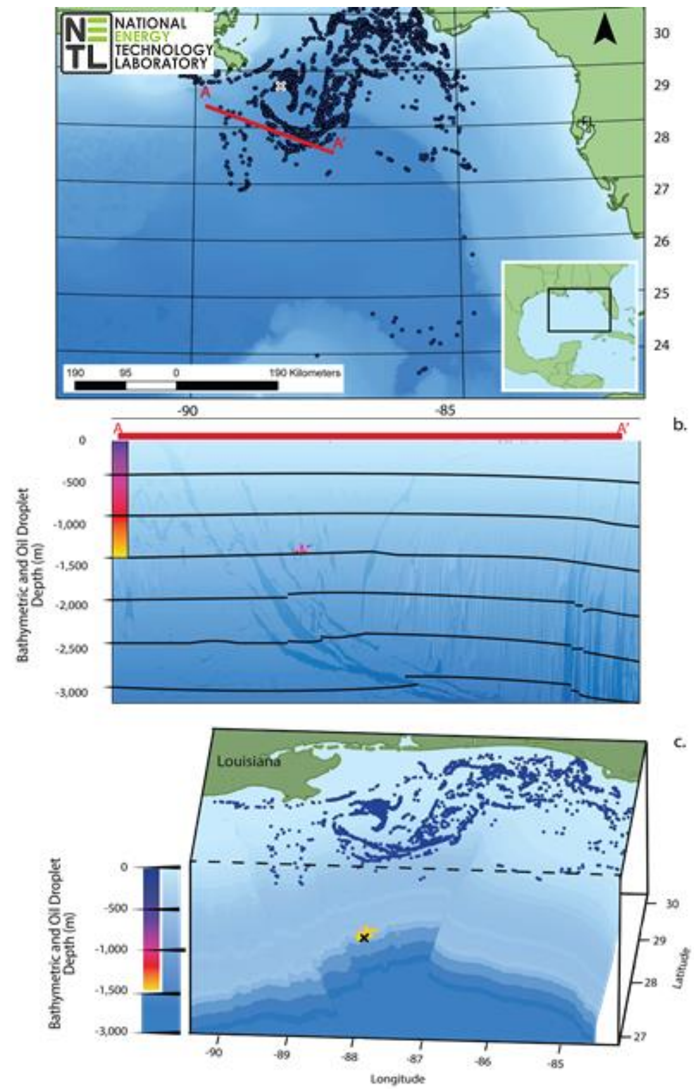
Significantly less oil made it to the surface than the Johansen et al. 2013 simulations.

The majority of oil stayed at depth.

- Untreated spread out into intrusion layers similar to Johansen et al. with treatment.
- Nearly all treated remained at depth.



Untreated



Treated

Subsea Dispersant Modeling Key Takeaways

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- Literature review revealed a strong correlation between oil viscosity and effectiveness of dispersant treatment.
- Droplet Size Distributions simulating dispersant application in BLOSOM closely match published and experimental results.
- A greater amount of oil was sequestered below the surface when simulated treatment was applied.
- PNNL2017 distributions were about an order of magnitude smaller than J2013.
  - This is due to experimental conditions, future work is needed to expand these results to ambient conditions.

BLOSOM is the only Open Source model that can simulate dispersant application subsea.

Products to date:
Updated BLOSOM build, https://edx.netl.doe.gov/blosom

Summary of Key Findings

- Changes in droplet size may not impact rates of biodegradation, but will impact oil migration
- The effect of pressure on microbial biodegradation is variable, but reduced temperature (also found in deep water) has a predictable effect of depressing biodegradation
- The presence of sediments and particulates can affect droplet size due to the formation of OPAs
- Blowout simulation experiments involving the rapid depressurization of oil found the following:
  - Depressurization leads to the atomization and emulsification of a fraction of the oil without the use of dispersants.
  - The addition of a dispersant resulted in a greater volume fraction of the oil having smaller droplet sizes.
  - Matching the temperature of the dispersant to the oil did not appear to affect the outcome.
  - Premixing dispersant with the oil (optimal mixing) rather than injecting the oil into the plume did not appear to affect the oil droplet size distribution.

Findings and Next Steps

- The ability to conduct high-pressure studies and to examine pressurized fluids (including oil) without depressurizing and thus physically altering the sample remains challenging.
- The physical constraints and limitations of tank experiments will invariably produce DSDs of a different scale than are produced by a full-scale blowout.
  - Challenges therefore exist in understanding how to properly establish equivalencies of scale between the experimental parameters and full scale ‘real world’ parameters, and for how to transform data and observations from an experiment to the equivalent real-world scale.
  - Finding the proper extrapolation method for the lab results from PNNL is therefore encouraged as a direction for future research.
- Another important direction for future research is simulating the evolution of the initial DSD (known as a dynamic DSD) to capture variations in size as the blowout evolves within the ocean, and at its surface.

Questions?

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