# OCEANS PROTECTION PLAN

# Environmental Significance of Oil Particle Interactions in Oil Spill Response

Kenneth Lee[1], Michel Boufadel[2] and Lin Zhao[2]

[1]Fisheries and Oceans Canada
[2]New Jersey Institute of Technology

# Oil Particle Interaction

- There is a renewed interest in oil particle interactions due to its apparent significance in the mediation of oil spill impacts that was highlighted by reports published in 1995 by Jim Bragg (Exxon Mobil) linking the recovery of oiled low-energy intertidal environments to the formation of "clay-oil flocculation" which enhanced the physical dispersion of the residual oil.
- Other terms for this general process include: oil mineral aggregates (OMA); oil sediment aggregates (OSA); oil suspended particulate matter aggregates (OSAs); oil particle aggregates (OPA) that may also include organic matter.
- Recent descriptions of aggregates with organic matter (e.g. bacteria, phytoplankton, detritus and extracellular polymers) have been described as marine oil snow (MOS).

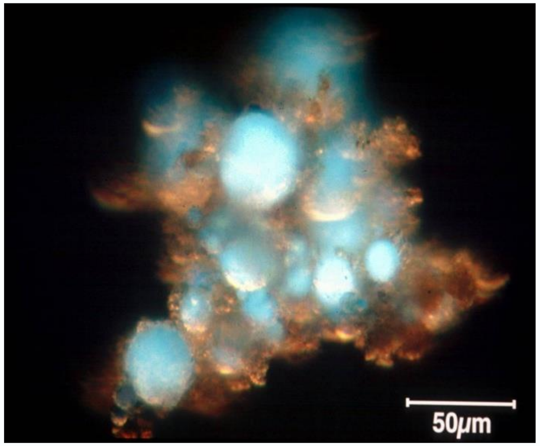
# MOSSFA and Subsurface Injection of Corexit

- Mesocosm study involving the subsurface injection of Corexit 9527 dispersed Prudhoe Bay crude oil
- Observed the association of oil droplets with biogenic material (phytoplankton and detritus) linked to a phytoplankton bloom
- Stimulatory effects on small zooflagellates and increased mortality on ciliates and appendicularians
- Corexit dispersed oil stimulated bacterial productivity rates by serving as substrates and/or by inducing the release of organic compounds from the indigenous microbial population
- A mass balance for 14C-hexadecane added to the test oil revealed that within 22 days, 3% was recovered in the suspended particulate fraction, 36% was respired as $CO_2$, 1% in the dissolved organic pool and 10% as sedimentary material.

Lee K, Wong CS, Cretney WJ, Whitney FA, Parsons TR, Lalli C, Wu J (1985) Microbial response to crude oil and Corexit 9527: SEAFLUXES enclosure study Microbial Ecology 11: 337-351

# Dispersion by Enhancement of Oil- Particle interactions

Naturally produced in high particulate estuarine and near shore waters

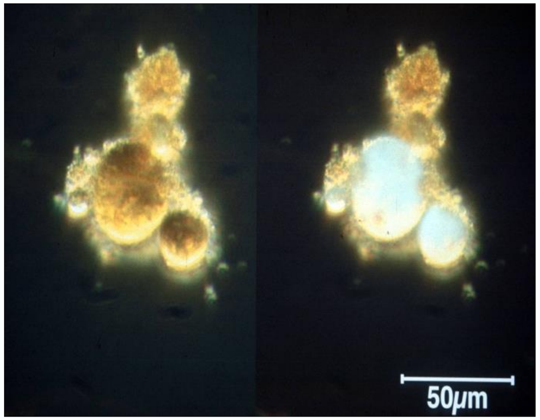



OMA occurs with naturally occurring suspended particles

- Mineral fines and associated organic fractions

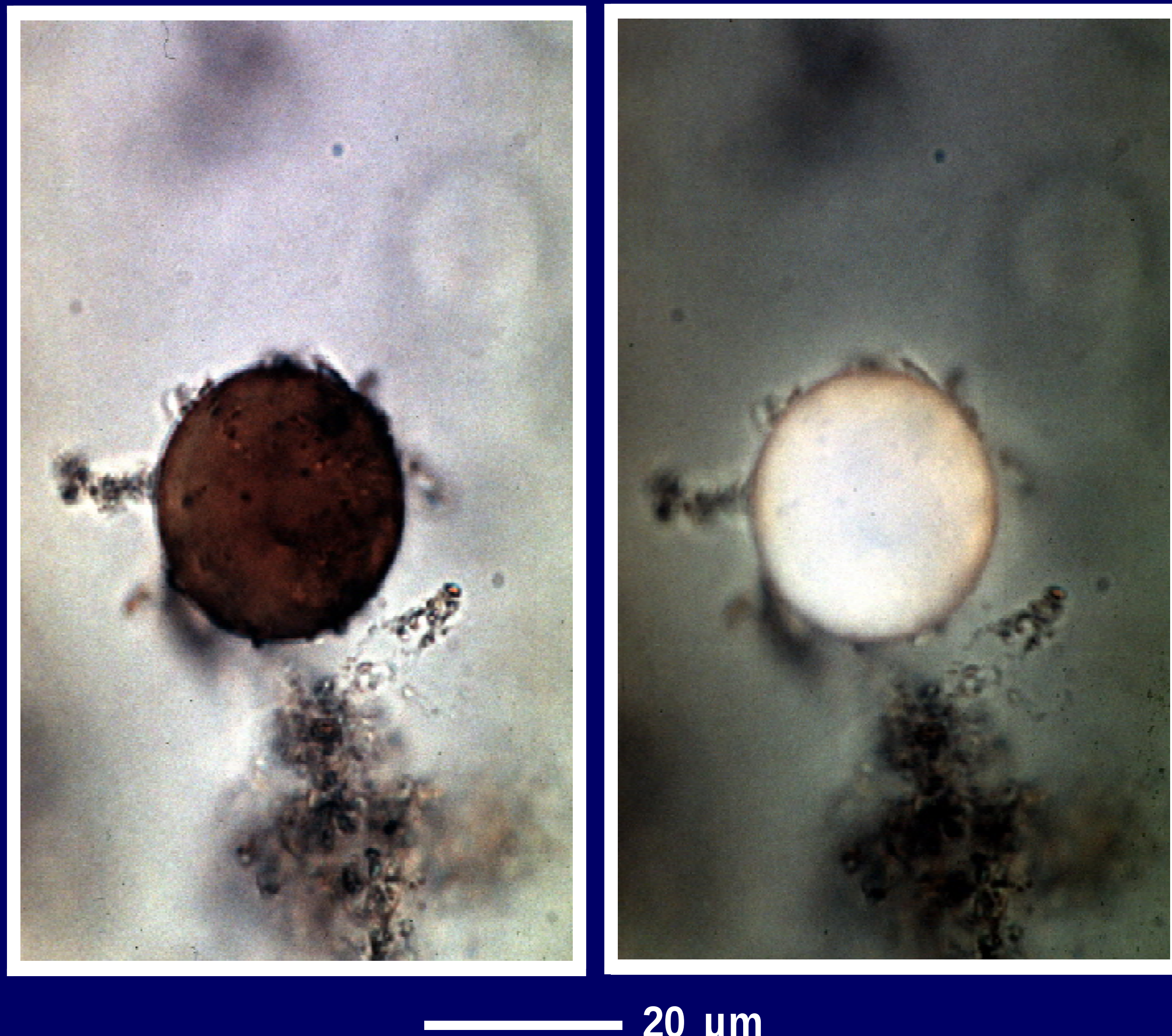
OMA changes fate and transport and effects of oil

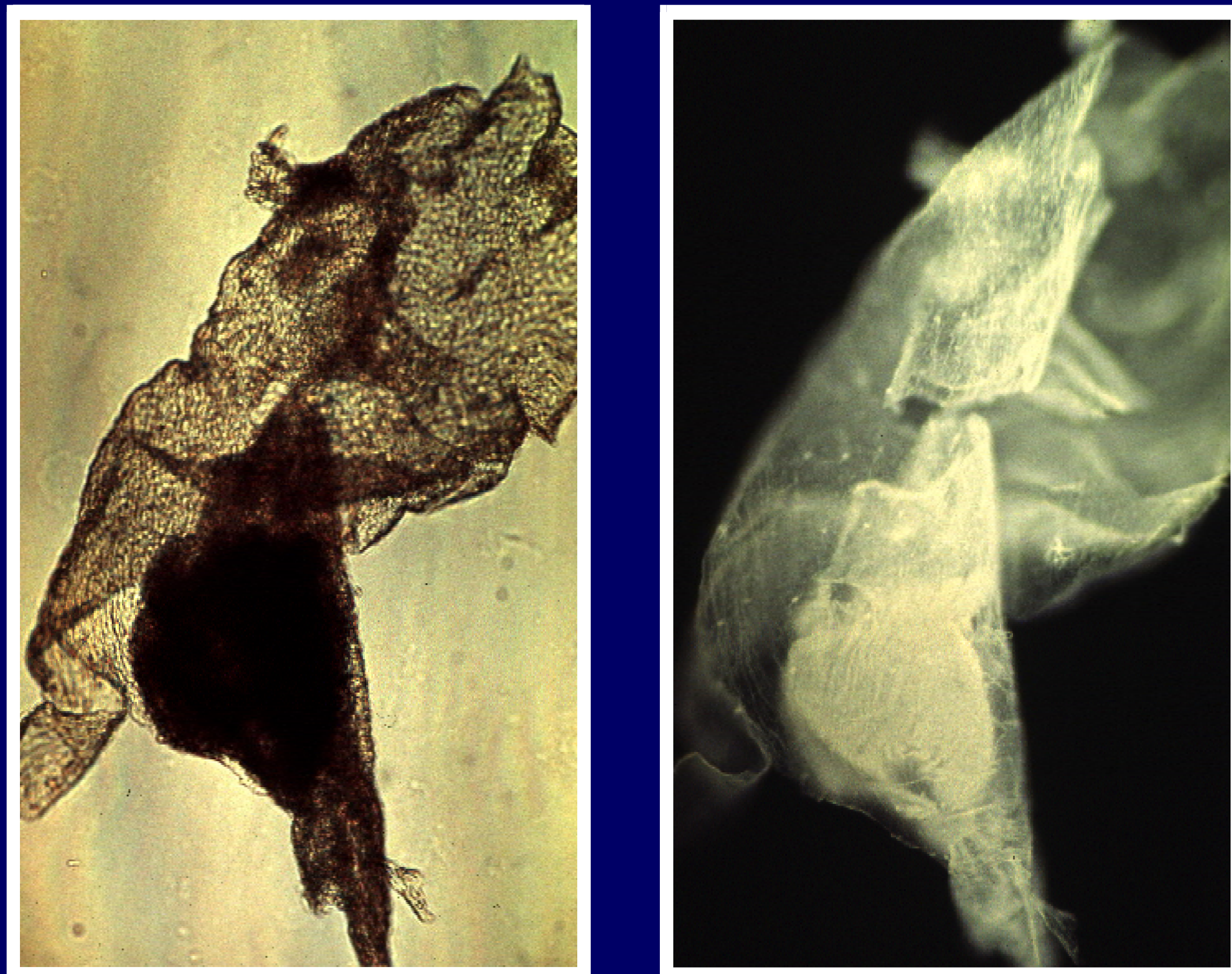
- Biodegradation rate
- Horizontal and vertical transport
- Potential biological effects



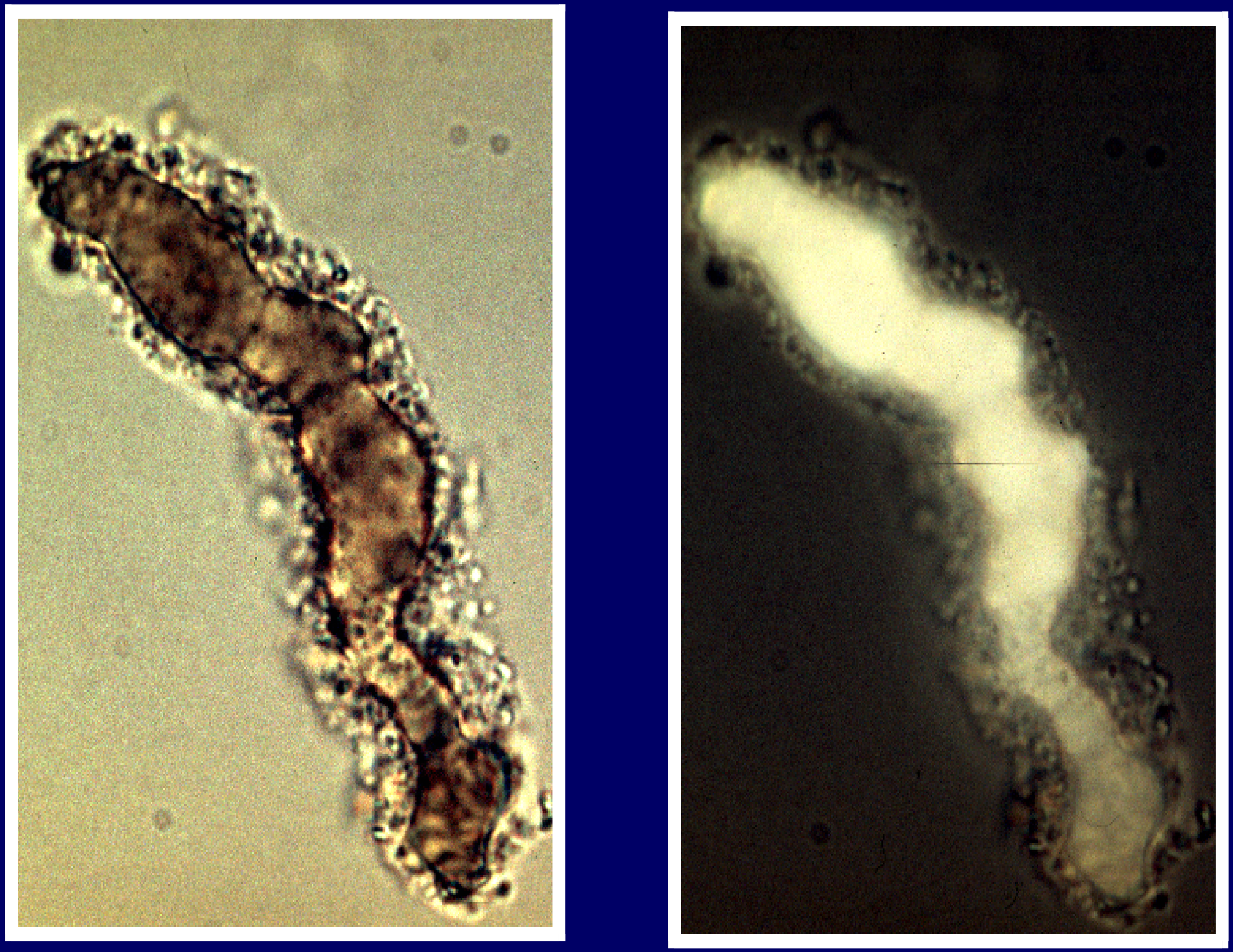
# Aggregate Type versus Mineral Type

| | |
|---|---|
| **Quartz** | **Droplet Aggregate** |
| **Kaolinite** | **Droplet Aggregate** |
| **Montmorillonite** | **Flake Aggregate** |
| **Kaolinite + Montmorillonite** | **Droplet + Flake** |
| **Natural sediment** (Svalbard, < 60 µm) | **Solid + Droplet** |


20 µm



50 µm



10 µm

# OPAs in Marine Systems

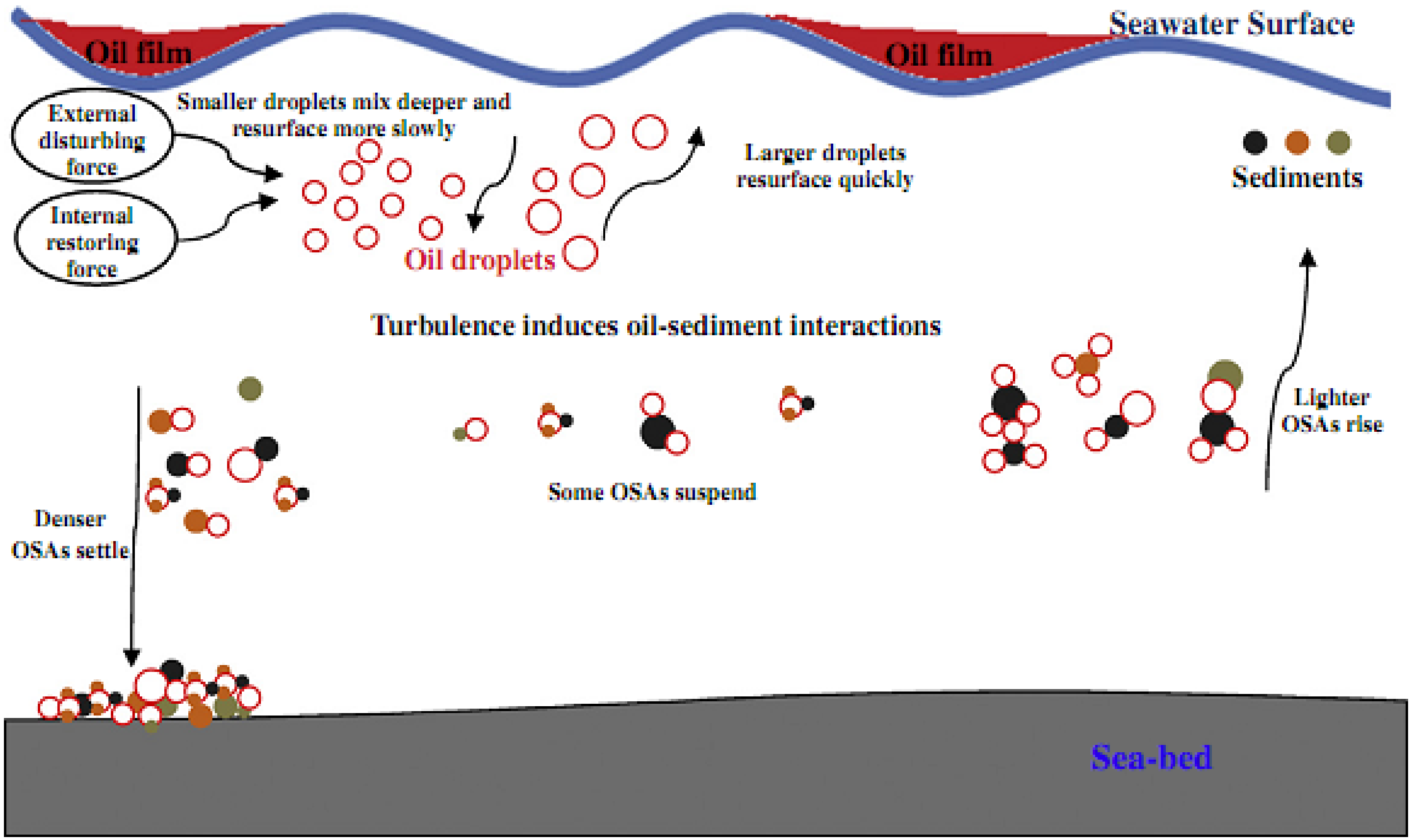
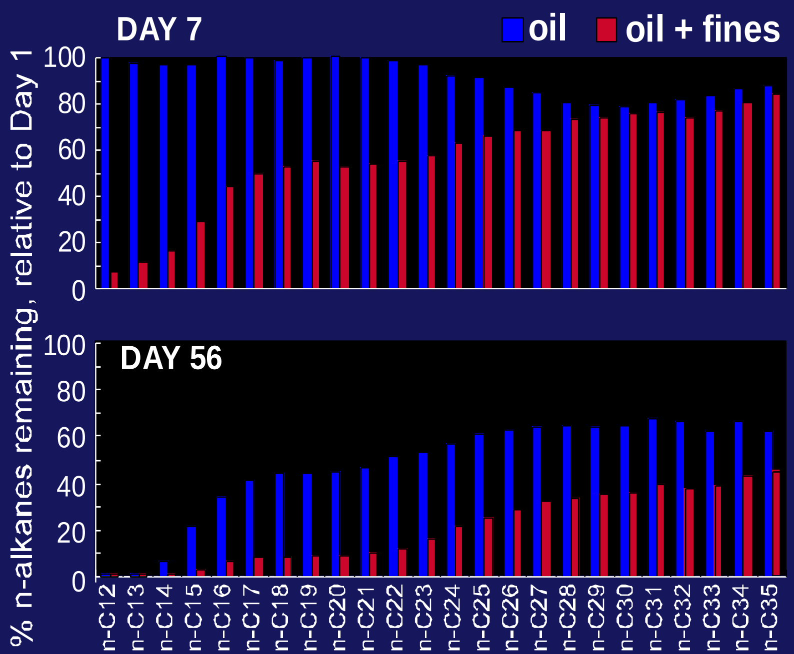
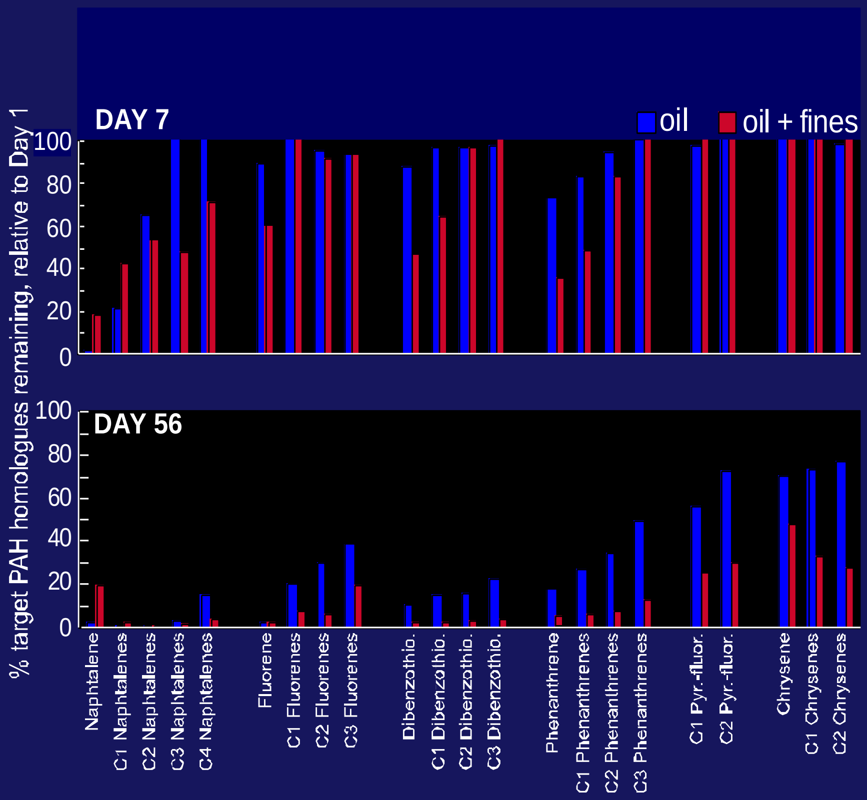



**Fig. 2.** Formation and movement of various types of OSAs in marine systems.

Y. Gong et al. /Marine Pollution Bulletin 79 (2013) 16–33

# Enhanced Biodegradation of n-alkanes and PAHs with Mineral Fines



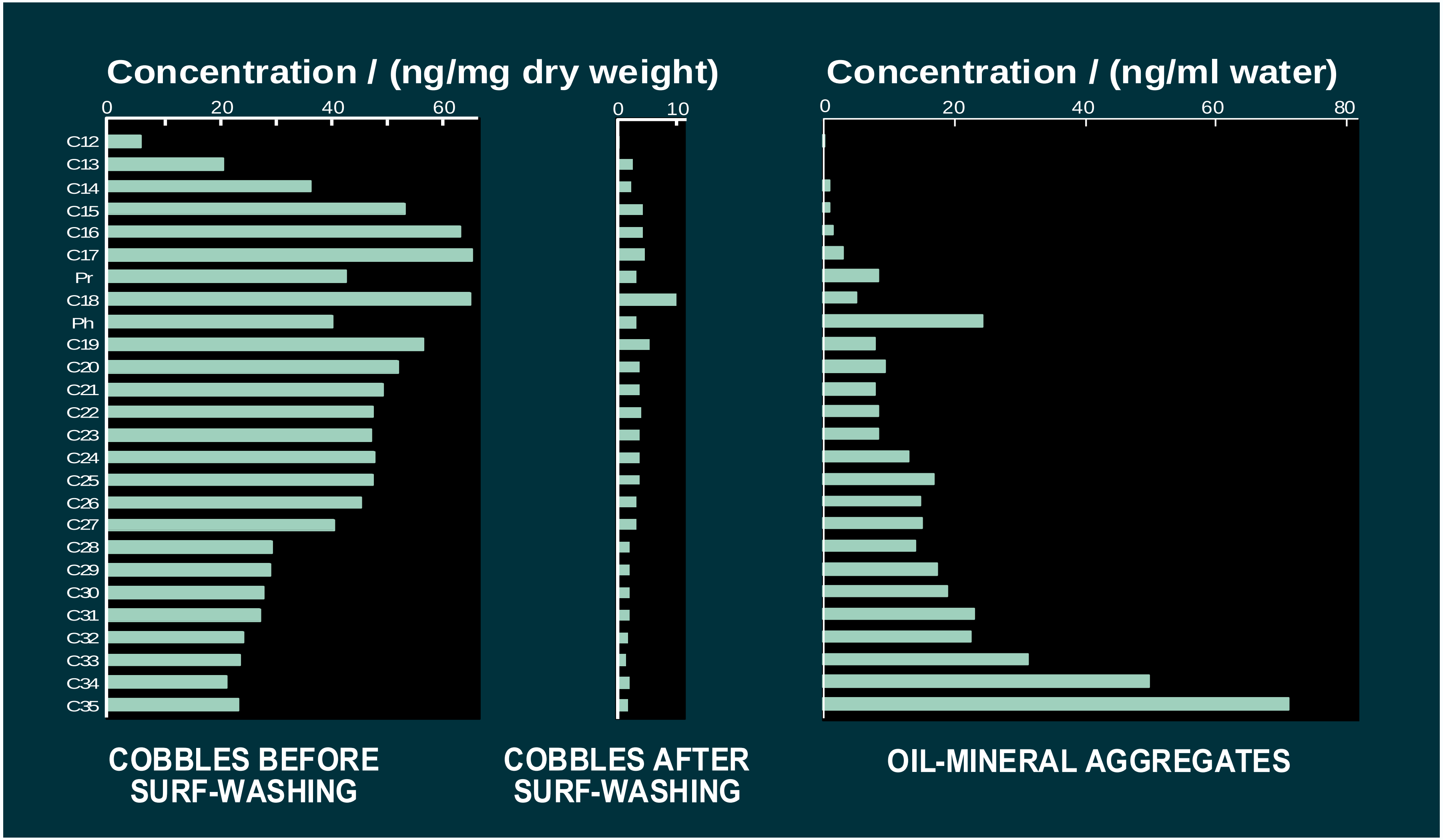
# OIL TRANSLOCATION

- An oil spill clean-up strategy based on the facilitation of oiled material transport from one environmental compartment to another that may include the enhancement of oil particle interactions
- Facilitates its physical recovery or enhances natural processes to break down the oil

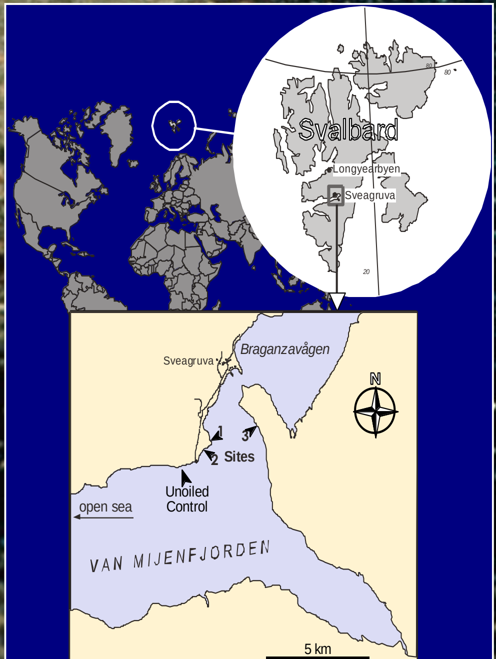
# The Sea Empress Oil Spill, UK

- Validation of Surf-Washing as an Oil Spill Countermeasure

# Oil components:
# n-alkanes, phytane and pristane



# Svalbard Field Trials




# Results from Svalbard Experiment

- About 3% of the oil removed from the beach is likely to have settled within 1 km of the oiled sites
- The oil lost from the sites has been biodegraded and/or dispersed over a large area
- Toxicity of residual oil was measured
  - in beach sediment samples
  - in sediment trap samples
  - in nearshore bottom sediments collected by divers
- Toxicity was below allowable limits for ocean dumping of dredged spoils.

# St. Lawrence Estuary Field Trial: DFO Science/CCG



Test effectiveness OMA formation as a oil spill countermeasure

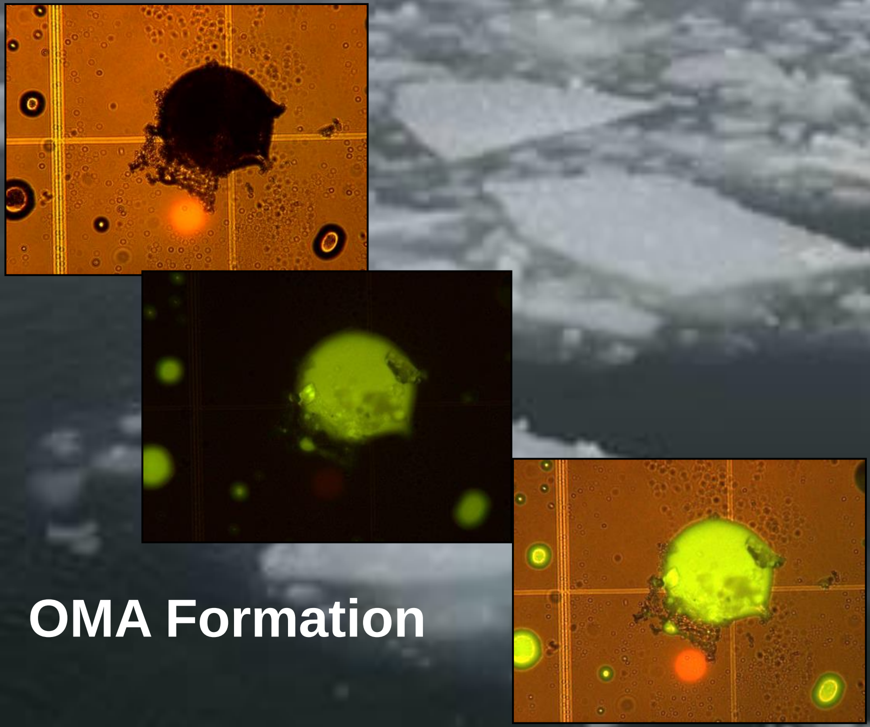
Fill the gap between lab and real-world application

Gain operational experience for larger scale field trails

* Controlled release of oil

# OMA Application and Mixing Treatment

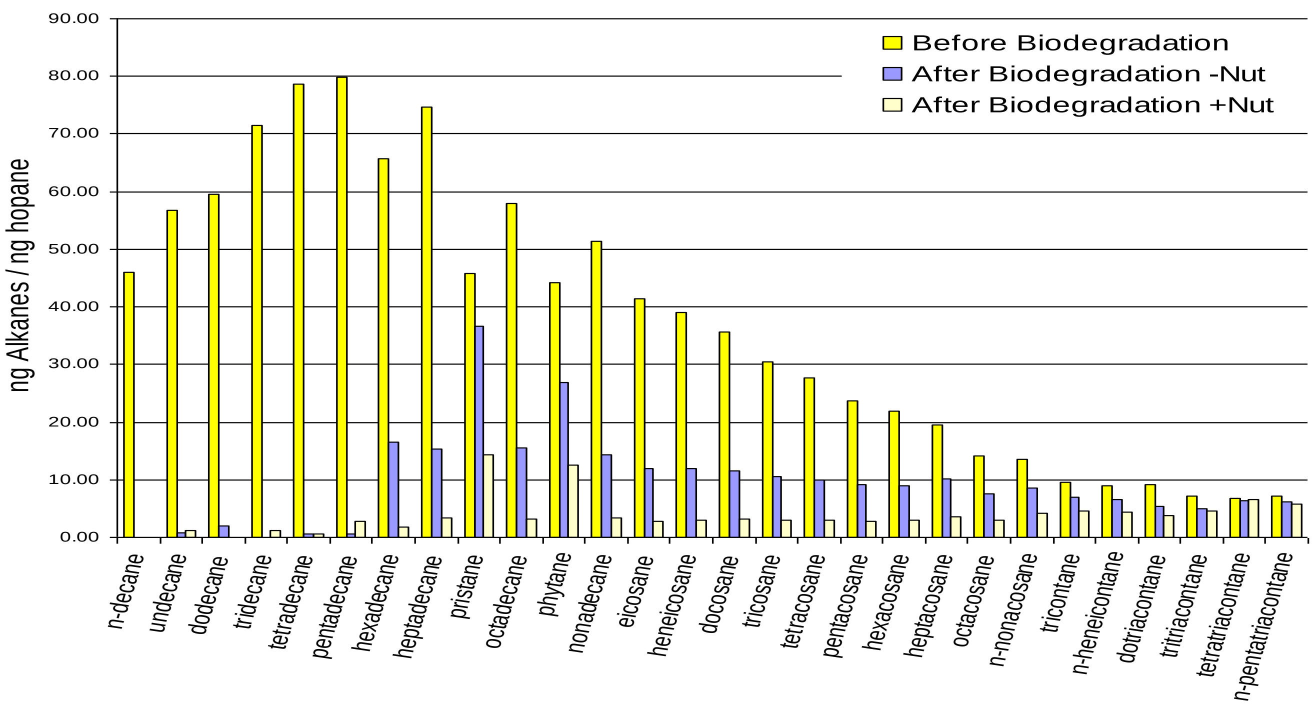
# Dispersion Efficacy with OMA



OMA Formation

# Biodegradation of Oil (n-alkanes)

Significant biodegradation verified by GC/MS analysis (analyates normalized to 17β(H), 21α(H)-hopane)




50 days at 0.5°C: 60% total Hydrocarbons; 75-88% total alkanes

55-65% PAHs

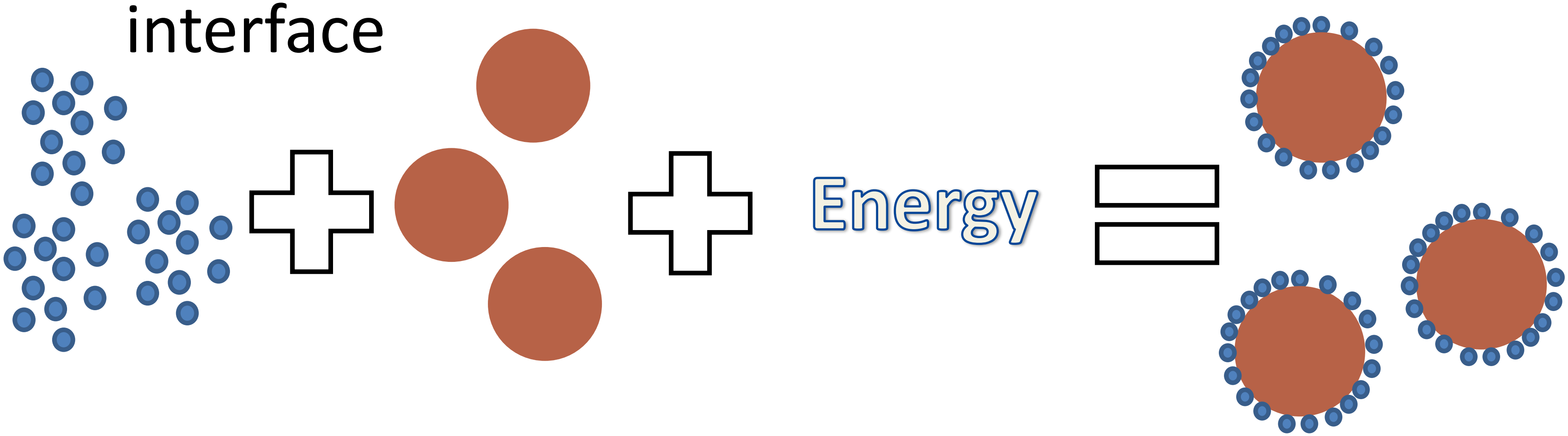
# MPRI Oil Translocation Program

- What are the operational conditions that support the transport of stranded oil to coastal waters via the formation of oil-mineral aggregates that can enhance natural processes to both disperse and biodegrade residual oil
- Conduct shoreline mesocosm studies to address knowledge gaps to allow for more strategic decision making regarding intervention or non-intervention responses.
- This work will provide more options to enable to accelerated attenuation and weathering of oil spilled near or on ice, effects of tidal forces and also understanding oil/particle interactions and the formation of oil-suspended particle aggregates

**Keywords:** oil particle interactions, shoreline characterization, guidance documents

# Mechanisms of OPA formation

- OPAs are oil and particle aggregates where the particles are adsorbed at the oil-water interface




Suspended particles

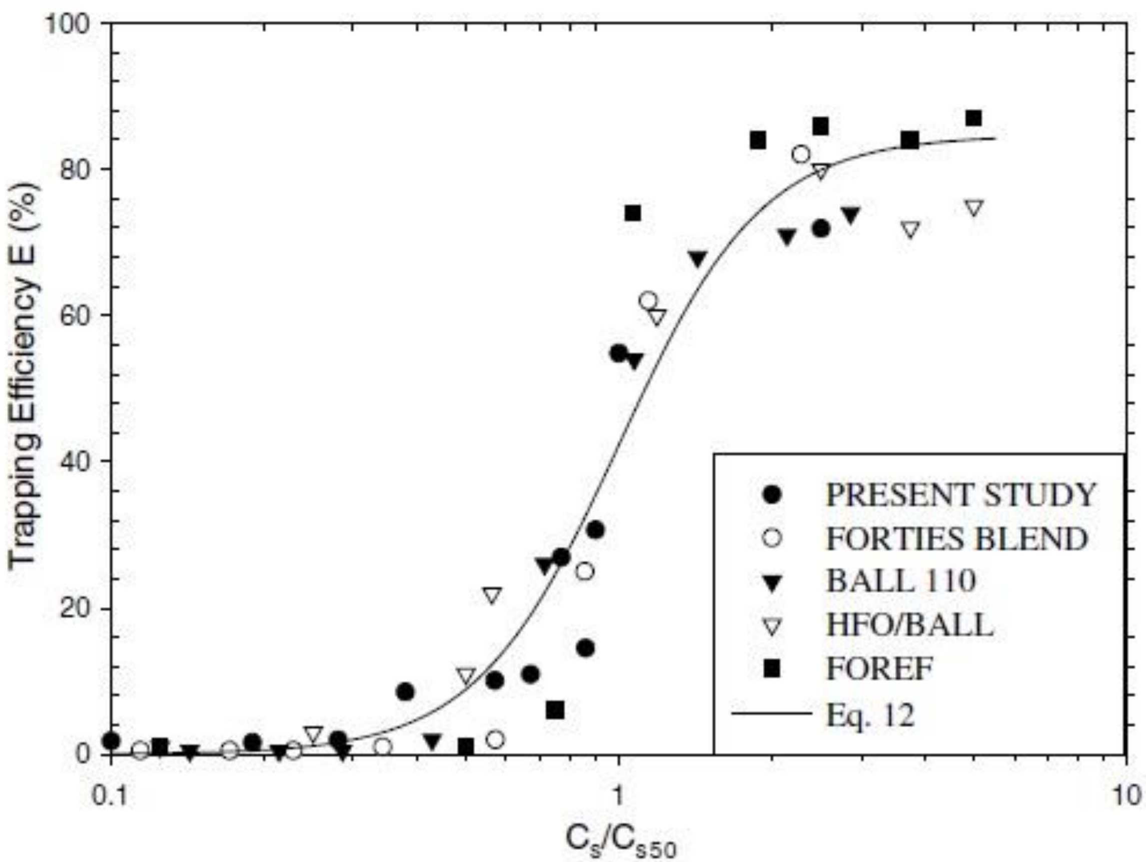
Oil droplets

OPA

# Existing Approach

Model the oil trapping efficiency E= Mass of Oil/Mass of OPA

$$E = \frac{E_{\max}\left(\frac{Cs}{Cs_{50}}\right)^n}{\left[1+\left(\frac{Cs}{Cs_{50}}\right)^n\right]}$$



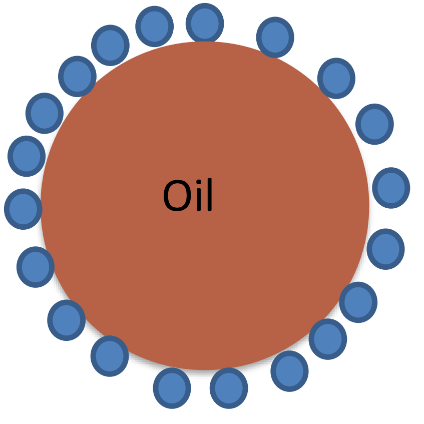
# A-DROP **Model for OPA Formation**

***Parameters:***

- *Oil*: density, viscosity, interfacial tension, size distribution, concentration.
- *Particles:* density, size and shape, hydrophobicity, concentration.
  Anything that adsorbs at the oil-water interface
  clay minerals, suspended particulate matter, bacteria, etc.
- Ambient condition: temperature, water salinity, mixing energy

## ***Main assumptions***:

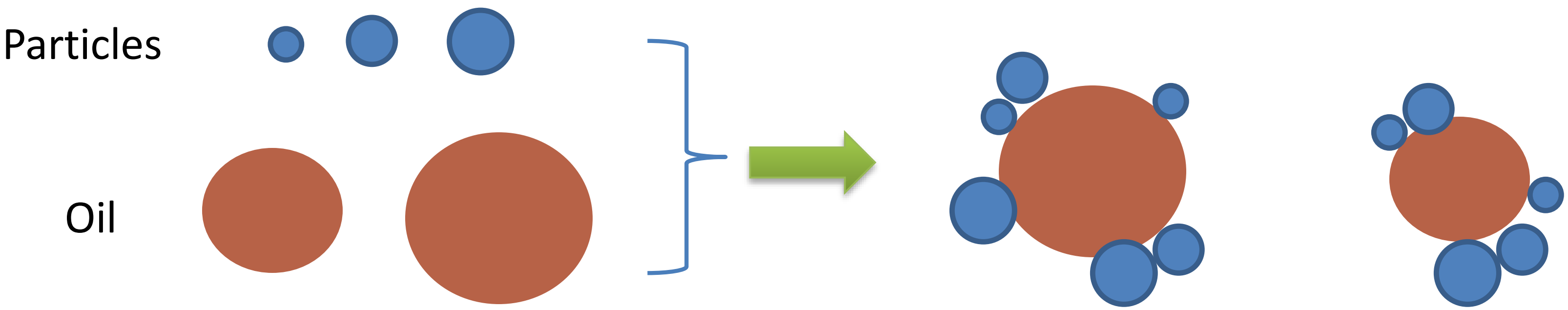
- Suspension of oil droplet and particles is well mixed in a turbulent flow regime.
- Oil droplets and particles have reached their final size distribution.
- Pickering emulsion is considered, and particles cover the oil droplet as a monolayer.
- The size of particles is much smaller than size of oil droplets
- No breakup of OPAs



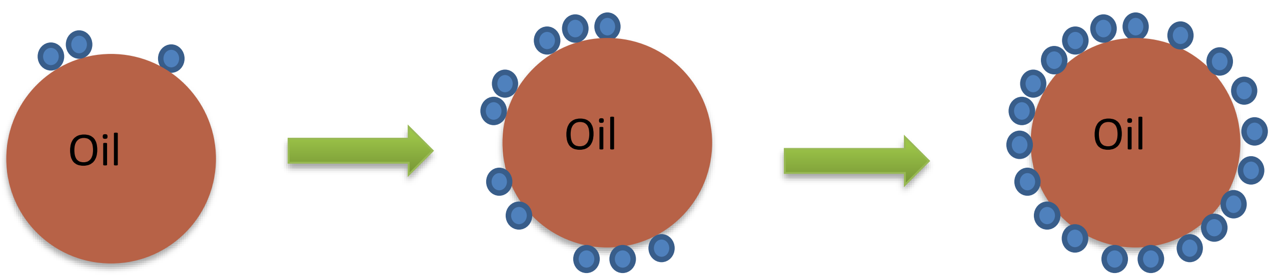
# A-DROP Model Development

***Predictions of:***

- ✓ Interactions of multi-size oil droplets, particles, and OPAs
- ✓ OPAs distribution in suspension and as negatively buoyant OPAs

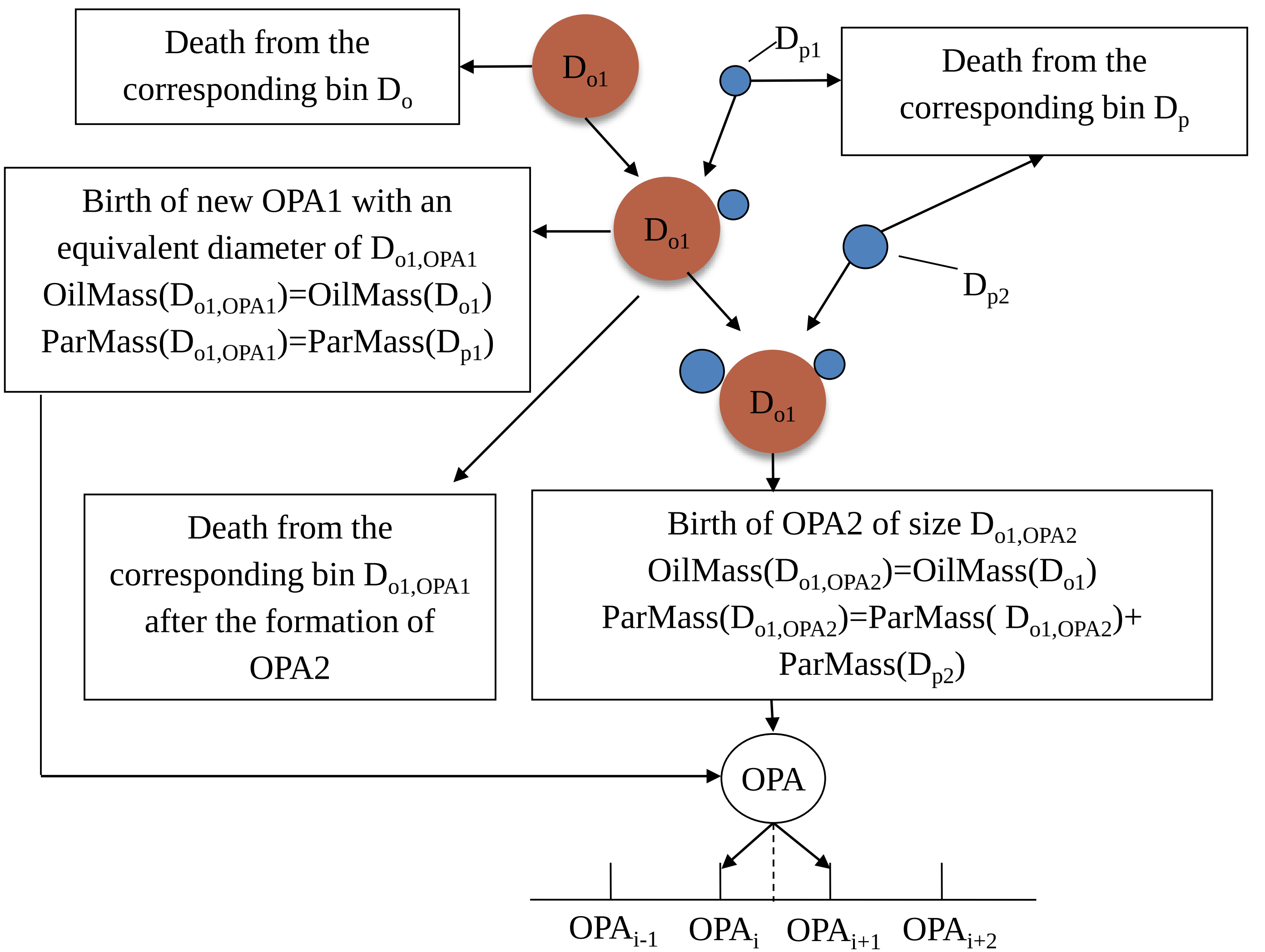



***Using the concept of coated area:***




**Coagulation rate decreases with the increase of coated area**

# OPA Formation



(2) # Governing Equations

Population balance model is constructed:

***Formation of OPAs***

$$\frac{dN(D_{OPA,m},t)}{dt} = \underbrace{\sum_{i=1}^{k}\sum_{j=1}^{n}}_{M_i+M_j=M_m} \alpha\beta N(D_{o,i},t)N(D_{p,j},t) + \underbrace{\sum_{i=1}^{m}\sum_{j=1}^{n}}_{M_i+M_j=M_m} \alpha\beta N(D_{OPA,i},t)N(D_{p,j},t) - N(D_{OPA,m},t)\sum_{i=1}^{n}\alpha\beta N(D_{p,i},t)$$

***Death of oil droplets and particles from the formation of OPAs***

$$\frac{dN(D_{p,i},t)}{dt} = -N(D_{p,i},t)\sum_{j=1}^{k}\alpha\beta N(D_{o,j},t) - N(D_{p,i},t)\sum_{j=1}^{l}\alpha\beta N(D_{OPA,j},t)$$

$$\frac{dN(D_{o,i},t)}{dt} = -N(D_{o,i},t)\sum_{j=1}^{n}\alpha\beta N(D_{p,j},t)$$

where N is the number concentration, D is the diameter, sediment particles denoted as ***p***, oil droplet denoted as ***o***, and oil-particle aggregates denoted as ***OPA***

# Governing Equations

- β is the collision frequency (Ernest et al., 1995):

$$\beta = \beta_{sh} + \beta_{ds} + \beta_B$$

***Turbulent shear:*** $$\beta_{sh} = \frac{1}{6}(D_i + D_j)^3(\varepsilon / \nu)^{1/2}$$

***Differential settling:*** $$\beta_{ds} = \frac{\pi}{4}\left(D_i + D_j\right)^2 \left|U_i - U_j\right|$$

***Brownian motion:*** $$\beta_B = \frac{2\kappa T}{3\rho_w \nu}\left(\frac{1}{D_i} + \frac{1}{D_j}\right)(D_i + D_j)$$

where ε is energy dissipation rate (Watt/kg), ν is kinetic viscosity of the continuous phase ($m^2/s$), U is the settling velocity which can be quantified as:

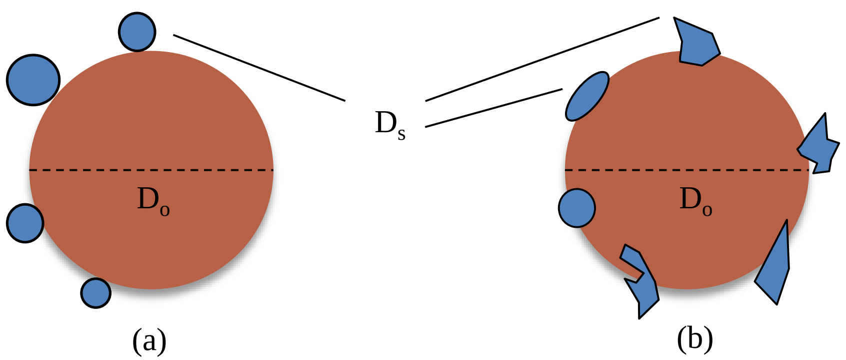
$$U_i = \sqrt{\frac{4g\left|\rho_p - \rho_w\right| D_i}{3 C_D \rho_w}}$$

# Governing Equations

- α is the coagulation efficiency:

$$\alpha(t)=\alpha_{sta}\left(1-\frac{\sum A_{p-proj}\text{ in OPAs}}{F_{SP}\sum A_o}\right)=\alpha_{sta}\left(1-\frac{\sum_{i=1}^{n} N(D_{p,i},t)\frac{1}{4}\pi D_{p,i}^2\text{ in OPAs}}{F_{SP}\sum_{i=1}^{k} N(D_{o,i},0)\pi D_{o,i}^2}\right)$$

where $A_o$ is the surface area of the oil droplet, $A_{p\text{-}proj}$ is the projection area of particles on $A_o$, and $\alpha_{sta}$ is stability ratio evaluated based on free energy analysis, $F_{SP}$ is the shape and packing factor.

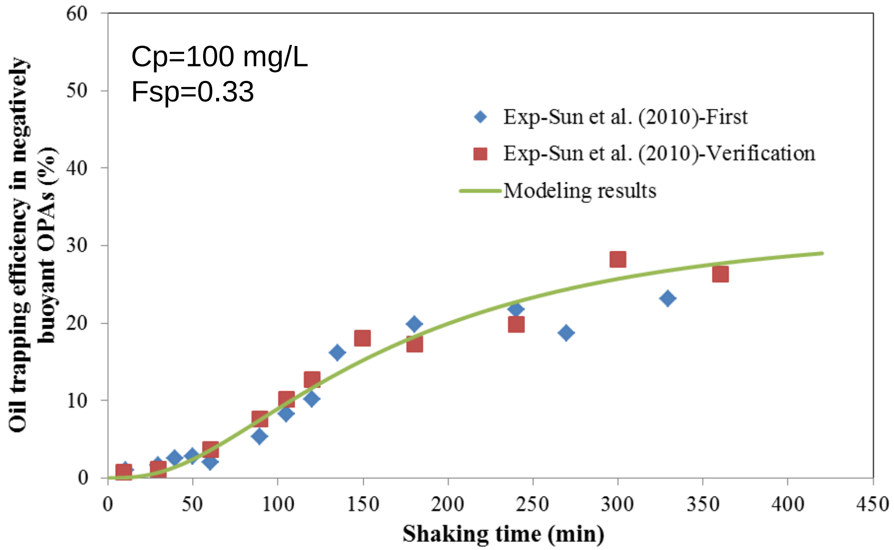


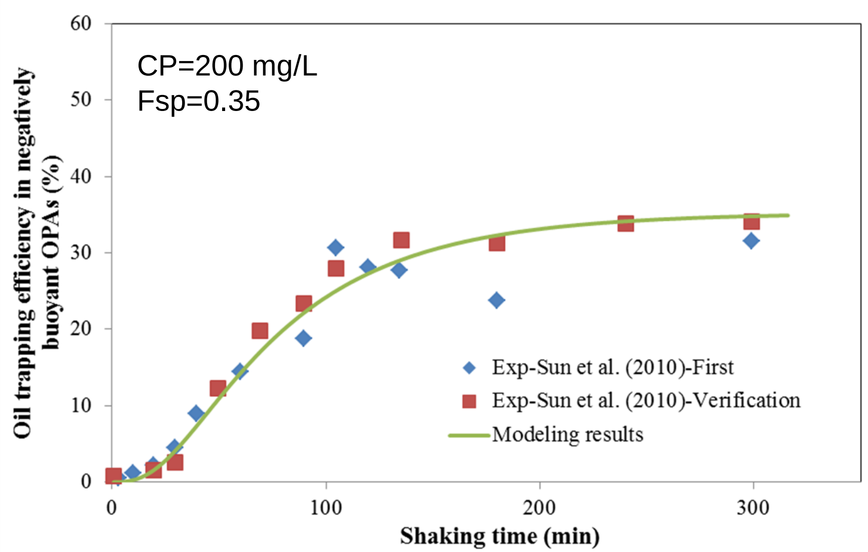
# Model Validation

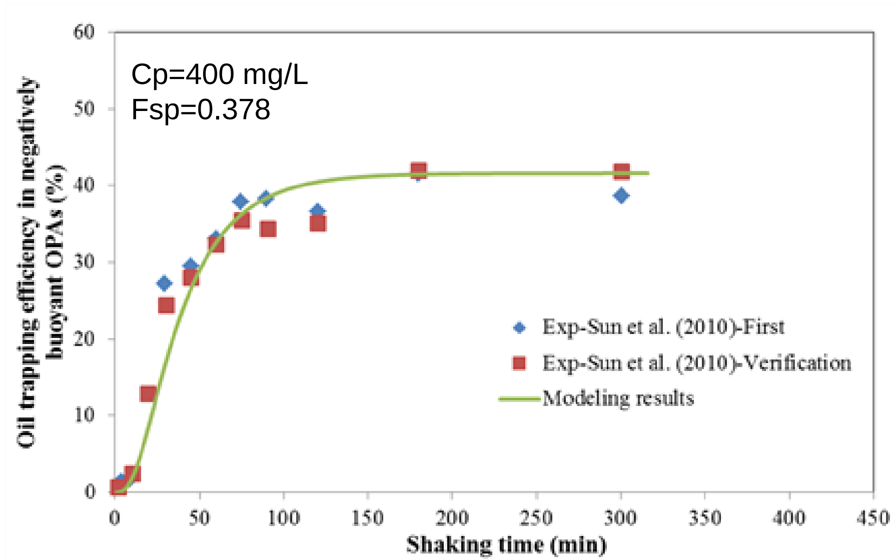
**Oil trapping efficiency (OTE) vs. Shaking time**

Particle concentration:

$C_p$=100, 200, 400 mg/L



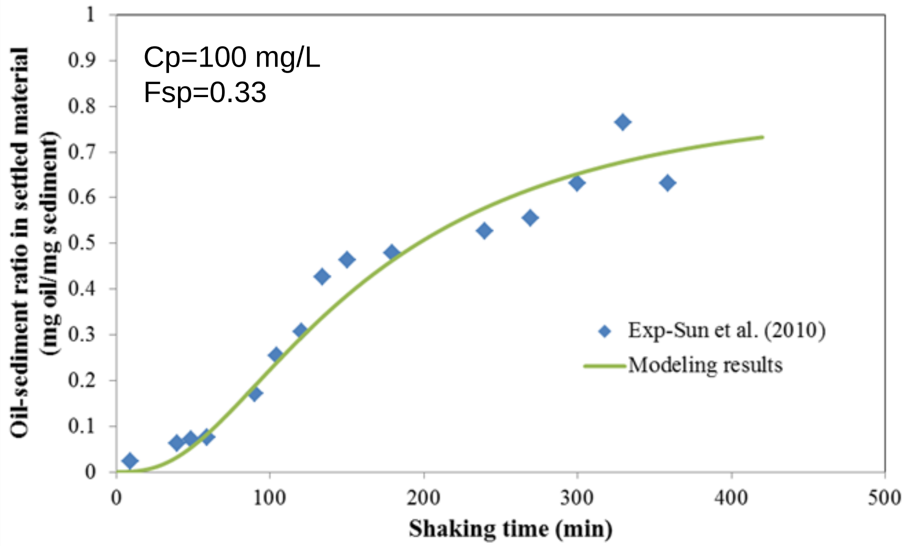

Experimental data were obtained from Sun et al./Marine Pollution Bulletin 60 (2010)/1701-1707

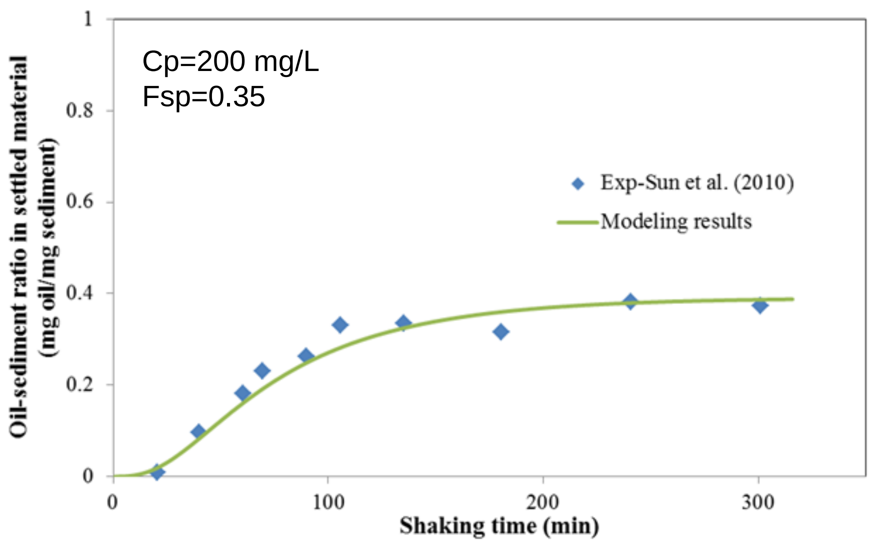
# Model Validation

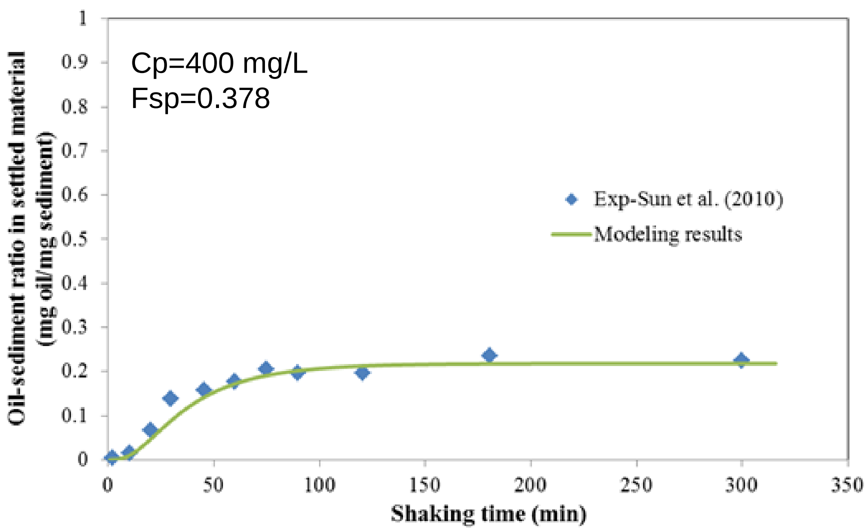
**Oil to sediment ratio (OSR) vs. Shaking time**

Particle concentration:

$C_p$=100, 200, 400 mg/L



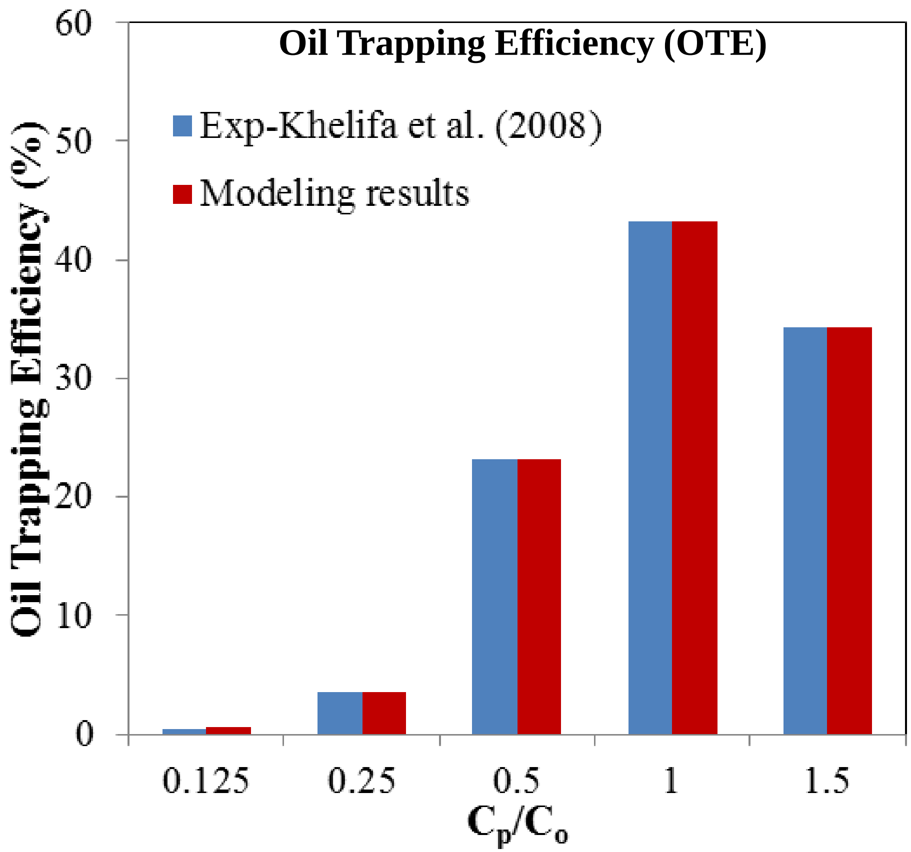



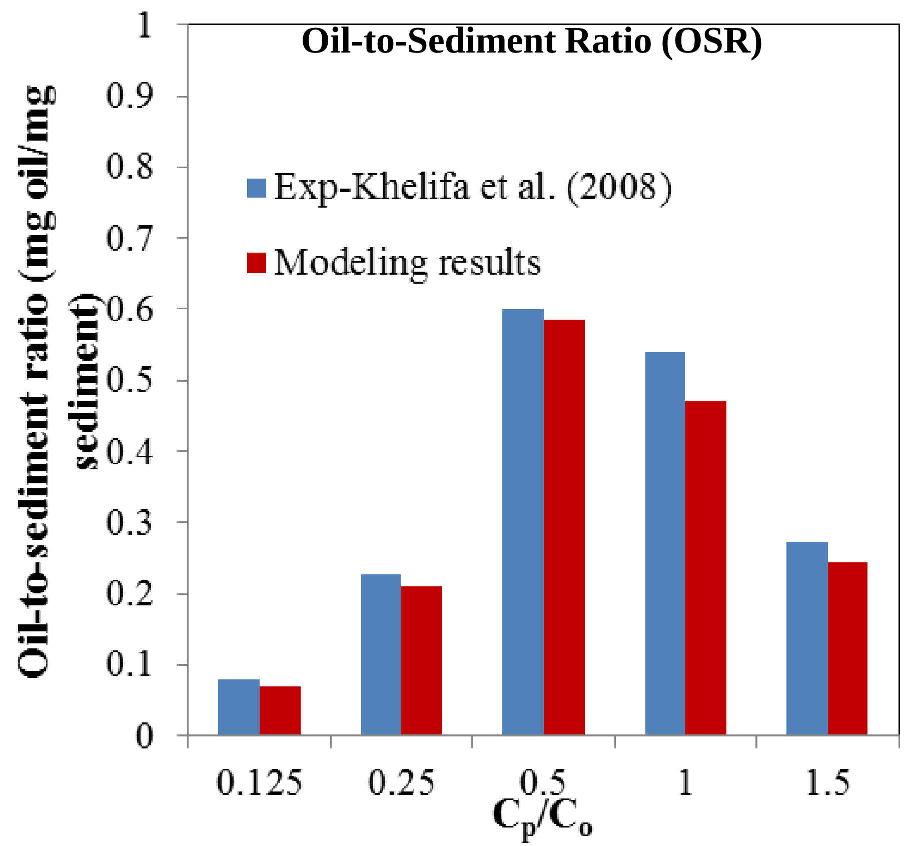




Experimental data were obtained from Sun et al./Marine Pollution Bulletin 60 (2010)/1701-1707

# Model Validation

Comparison with experimental data from Khelifa et al. (2008)

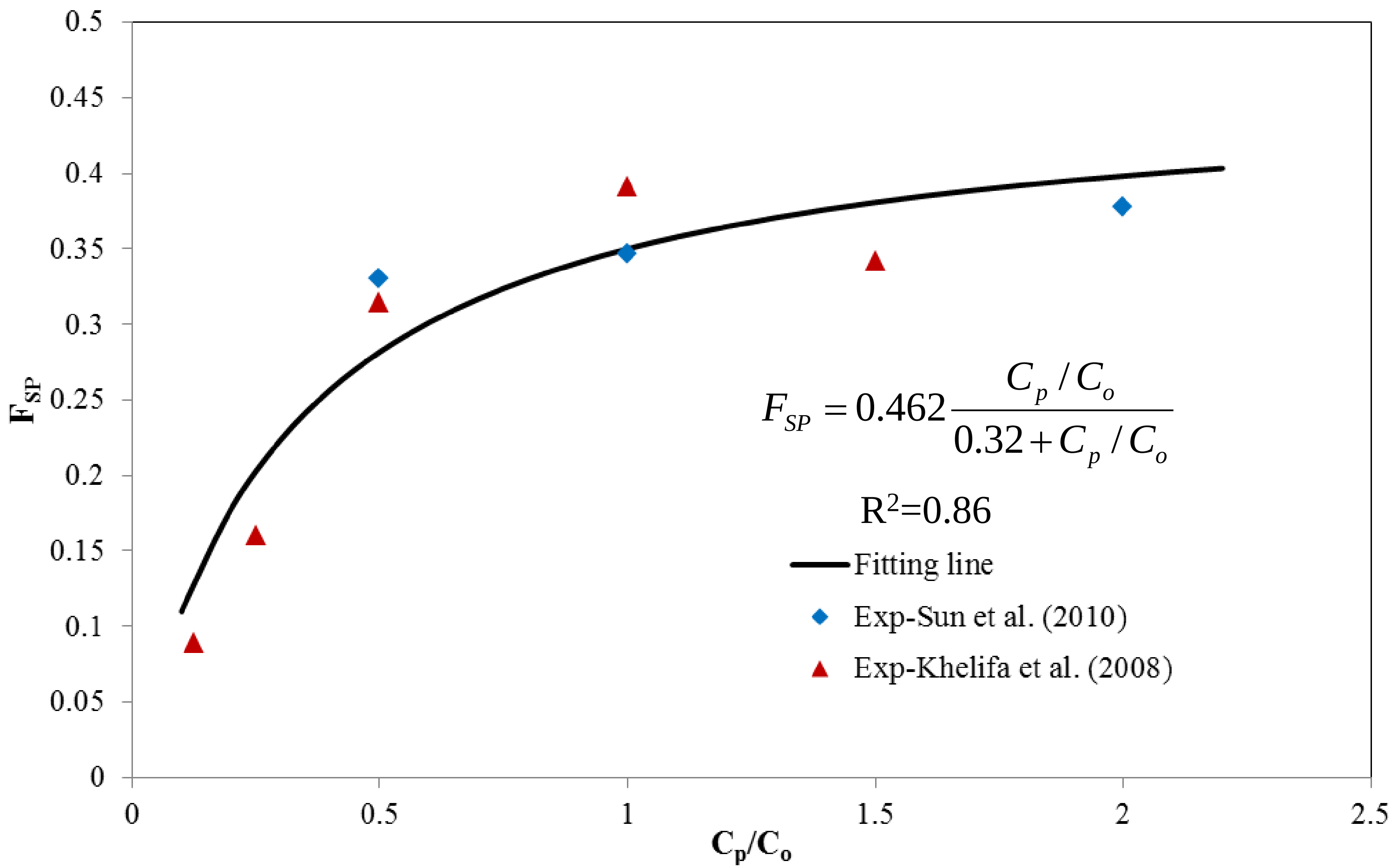



* $C_p/C_o$ = particle concentration/oil concentration

Experimental data were obtained from Khelifa et al./Report from Coastal Response Research Center .

# Packing on droplet increases with particle concentration




$C_p/C_o$ = particle concentration/oil concentration

# Oil dispersion

**Michel C. Boufadel, Lin Zhao**

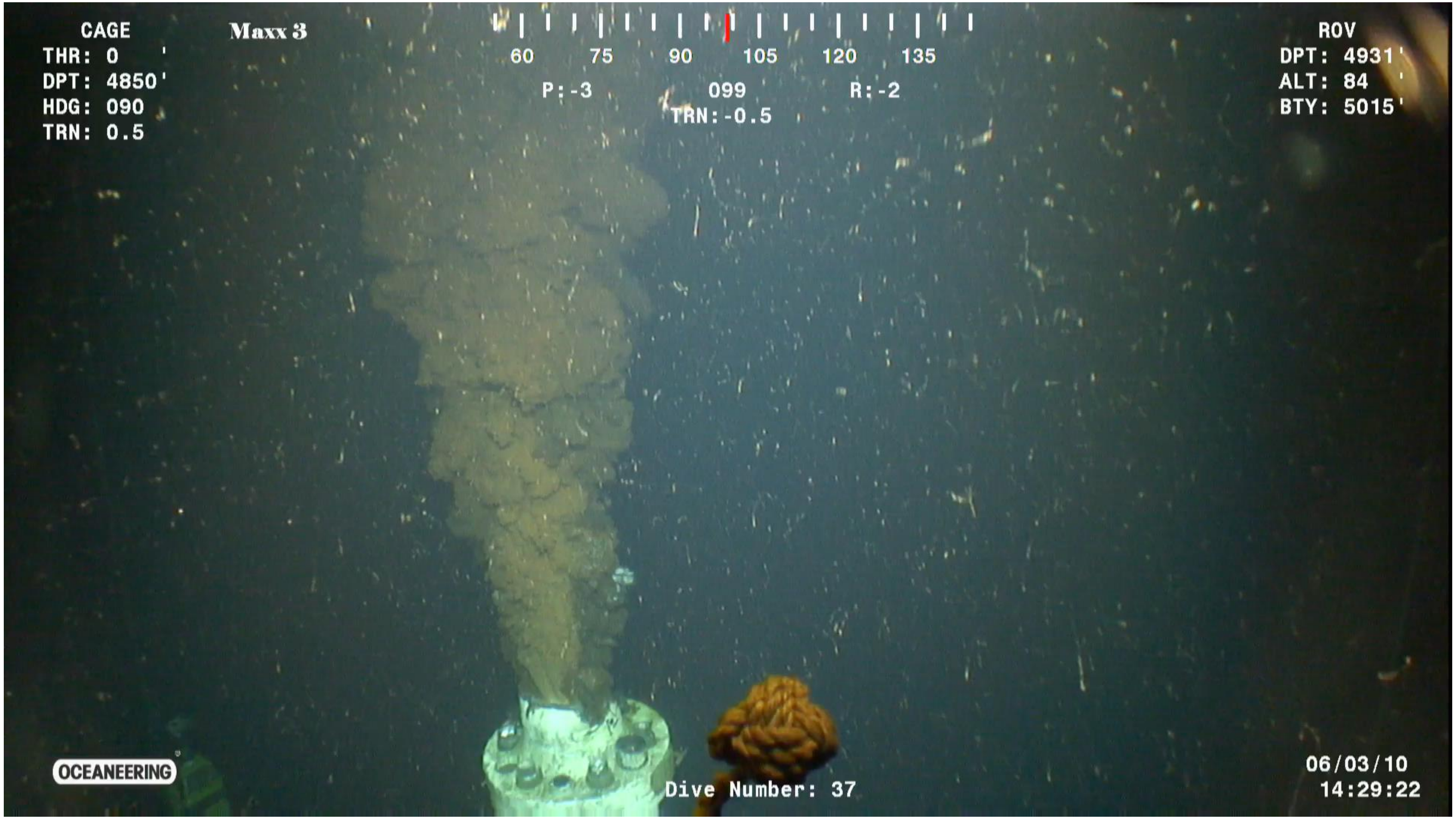
**Center for Natural Resources**
**The New Jersey Institute of Technology**
**Newark, New Jersey 07102**

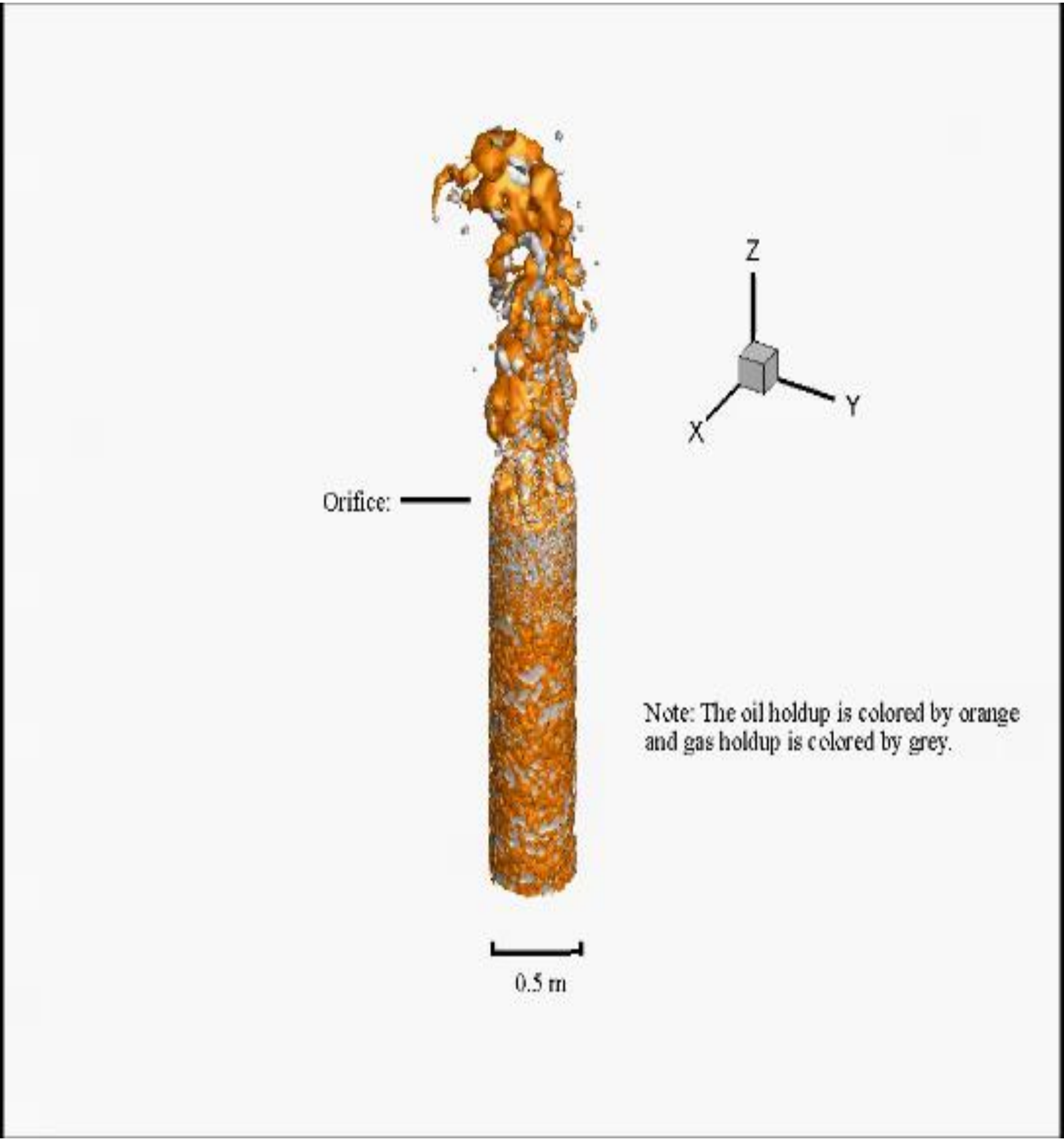
**boufadel@gmail.com**
**http://nrdp.njit.edu**

**And**

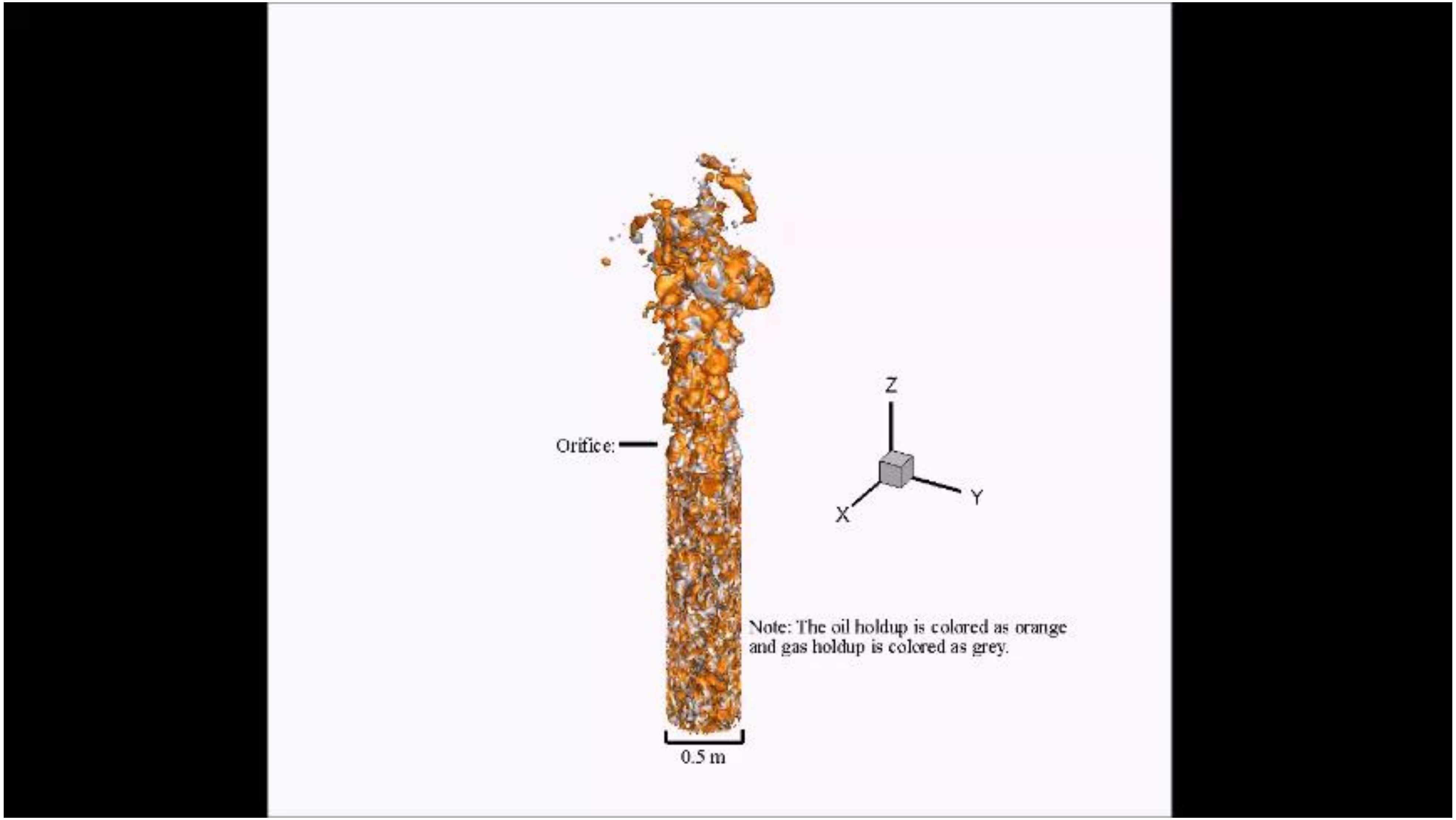
**Kenneth Lee, Department of Fisheries and Oceans, Canada**

# MC252 Wellhead

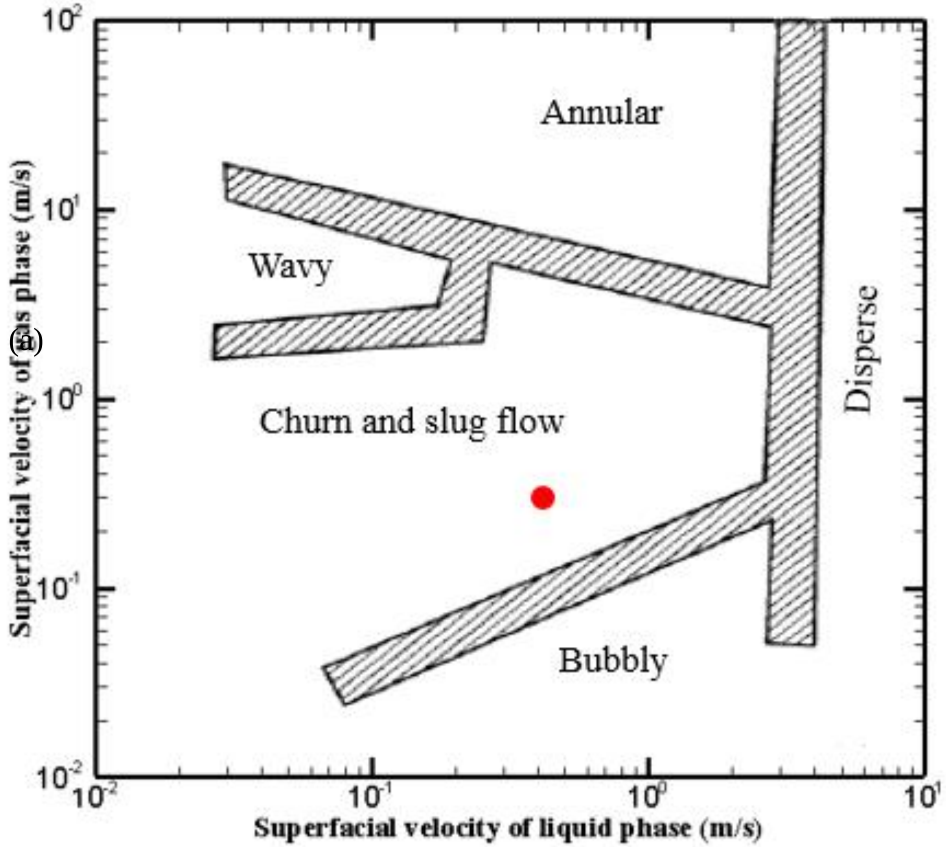


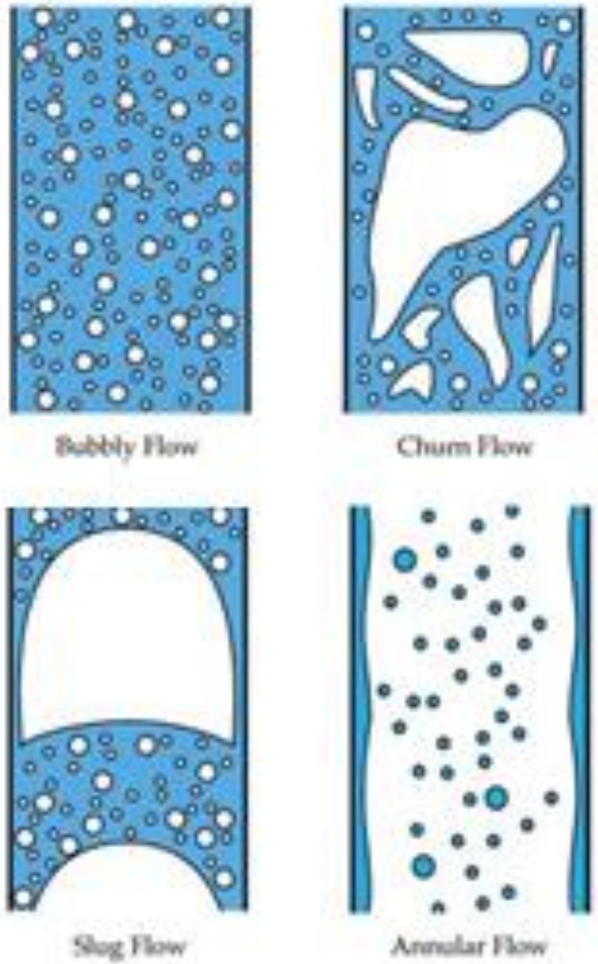

Z
Y
X
Orifice:
0.5 m
Note: The oil holdup is colored by orange and gas holdup is colored by grey.

Gas at 45% of volume and live oil at 55% of volume.  Churn Flow



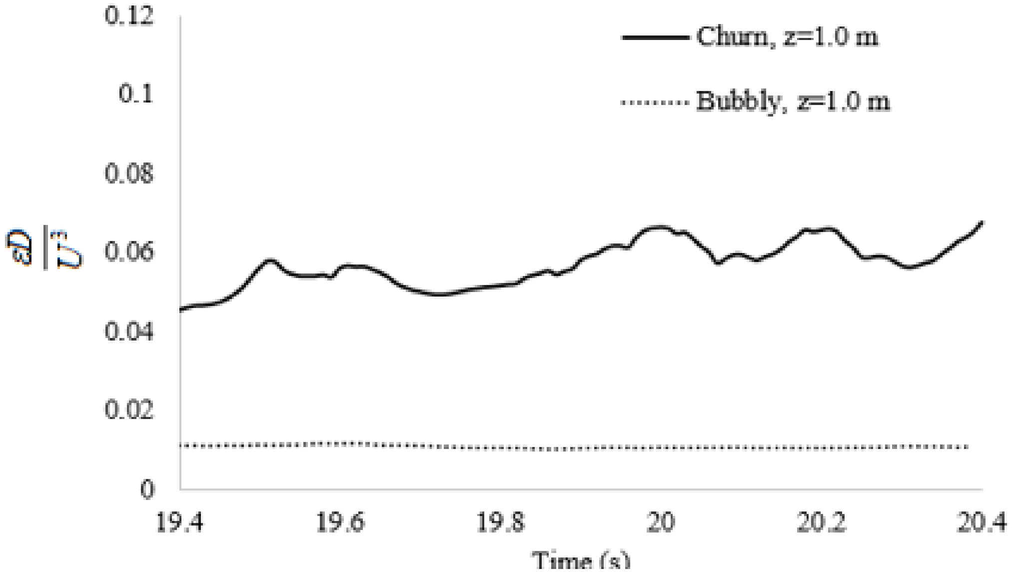

Boufadel, et al., Geophysical Research Letters, 45(4), February 2018.


Annular
Wavy
(a)
Churn and slug flow
Disperse
Bubbly
Superfacial velocity of gas phase (m/s)
Superfacial velocity of liquid phase (m/s)
$10^{2}$
$10^{1}$
$10^{0}$
$10^{-1}$
$10^{-2}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$10^{1}$

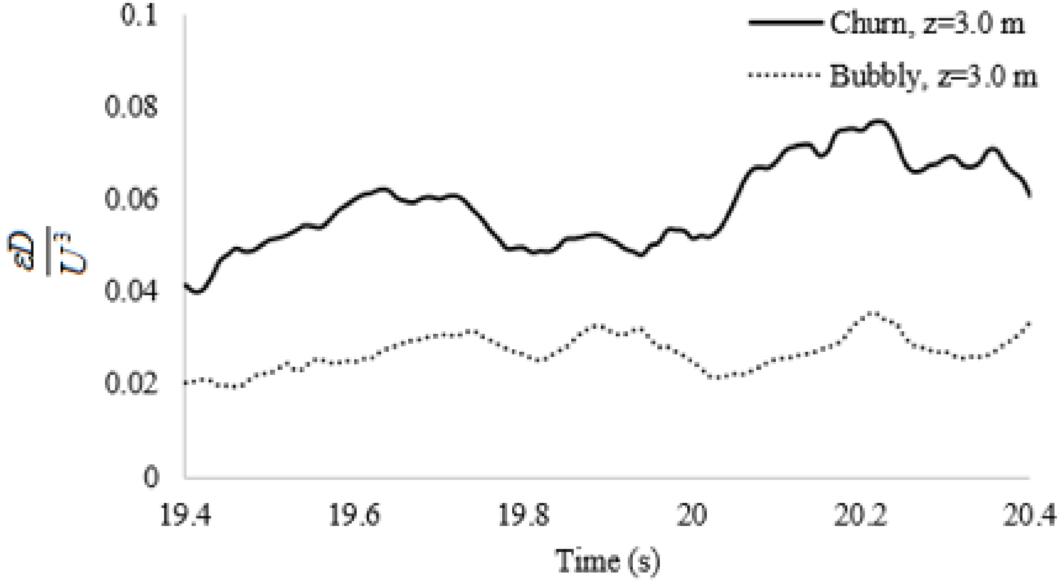

Bubbly Flow
Churn Flow
Slug Flow
Annular Flow


Bubbly flow

## Energy dissipation rate MC252




Within the riser (pipe)




At 1.0 m above orifice

Boufadel et al., Geophysical Research Letters, 45(4), February 2018.

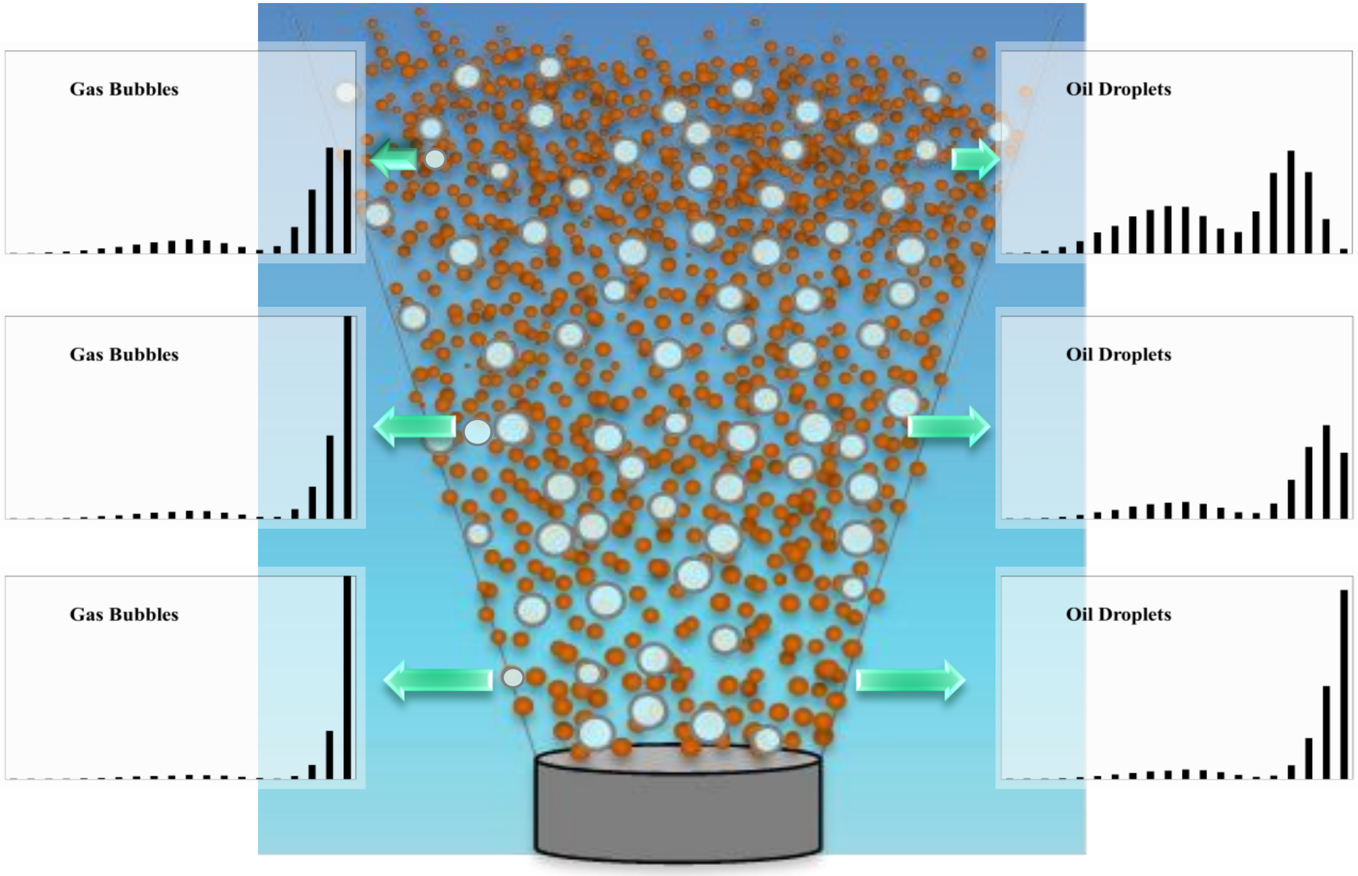
# Conclusions

The presence of gas should be considered not only at the orifice but within the riser.

If the regime is “churn”, the measured oil flow rate could be overestimated, and calculated droplet sizes could be overestimated.

Dispersant effectiveness in the presence of churn flow is not known.
No droplet model accounts for churn flow impact on droplet formation, and efforts are ongoing to calibrate VDROPJ to churn flow conditions.

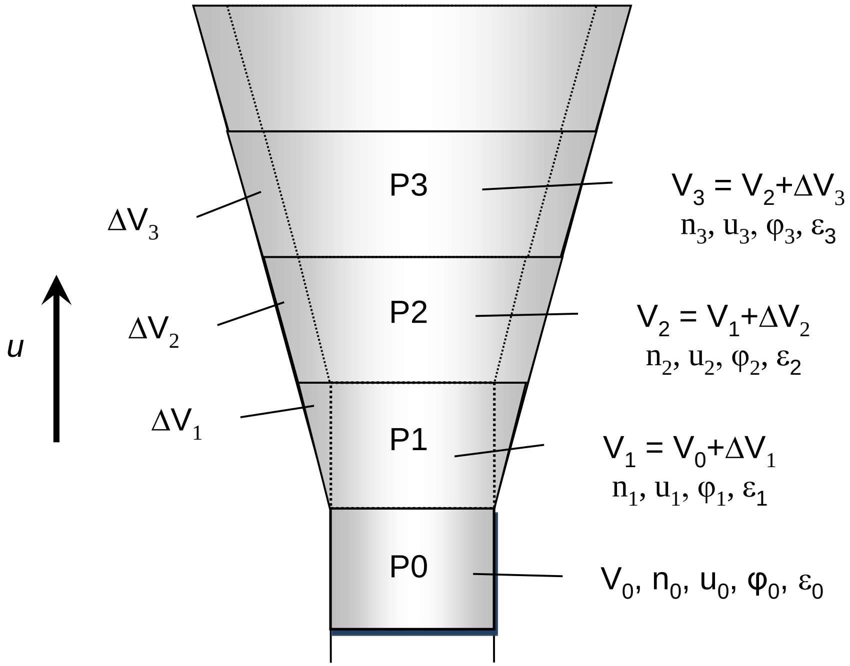
# Prediction of the oil droplets size distribution is key




Zhao, Boufadel, Socolofsky, Lee, et al., Marine Pollution Bulletin, 2017

# VDROP-J (J for Jet)

- Lagrangian method
- Following fluid parcels
- Energy dissipation rate and holdup decrease with evolution of the jets and plumes
- The number concentration of droplets is updated every time step




Zhao, Boufadel,Socolofsky, Lee., Nedwed et al. (2014), Evolution of droplets in subsea oil and gas blowouts, *Marine Pollution Bulletin*, 83(1): 58-69, 2014

Zhao L., Gao F., Boufadel M.C., King T., Robinson B., Lee K., Conmy R. Oil jet with dispersant: Macro-scale hydrodynamics and tip streaming. ***AIChE Journal*** 63, 5222-5234, 2017.

Gros J., Socolofsky S.A., Dissanayake A.L., Jun I., Zhao L., Boufadel M.C., Nelson R.K., Reddy C.M., Arey J.S. Petroleum dynamics in the sea and influence of subsea dispersant injection during Deepwater Horizon. ***Proceedings of the National Academy of Sciences*** 114, 10065-10070, 2017.

Zhao L., Shaffer F., Robinson B., King T., D'Ambrose C., Pan Z., Gao F., Miller R.S., Conmy R.N., Boufadel, M.C. Underwater oil jet: Hydrodynamics and droplet size distribution. ***Chemical Engineering Journal*** 299, 292-303, 2016.

Zhao L., Boufadel M.C., King T., Robinson B., Gao F., Socolofsky S.A., Lee K. Droplet and bubble formation of combined oil and gas releases in subsea blowouts. ***Marine Pollution Bulletin*** 120, 203-216, 2017.

Zhao L., Boufadel M.C., Lee K., King T., Loney N., Geng X. Evolution of bubble size distribution from gas blowout in shallow water. ***Journal of Geophysical Research: Oceans*** 121, 1573-1599, 2016.

Zhao L., Boufadel M.C., Adams E., Socolofsky S.A., King T., Lee K., Nedwed T. Simulation of scenarios of oil droplet formation from the Deepwater Horizon blowout. ***Marine Pollution Bulletin*** 101, 304-319, 2015.

Zhao L., Torlapati J., Boufadel M.C., King T., Robinson B., Lee K. **VDROP**: a comprehensive model for droplet formation of oils and gases in liquids – Incorporation of the interfacial tension and droplet viscosity. ***Chemical Engineering Journal*** 253, 93-106, 2014.

Zhao L., Boufadel M.C., Socolofsky S.A., Adams E., King T., Lee K. Evolution of droplets in subsea oil and gas blowouts: development and validation of the numerical model **VDROP-J.** ***Marine Pollution Bulletin*** 83, 58-69, 2014.

# Ohmsett Wave Tank
# New Jersey

- The largest outdoor saltwater wavetank facility in North America
- 203 m long, 20 m wide, 2.4 m deep
- Filled with 2.6 million gallons (about 9800 $m^3$) of salt water

# Subsurface Oil Release in Ohmsett

- Conducted in June 2018
- Oil: Fuel oil #2
- Vertical oil release
- Bridge towing to dilute the plume for measurements

**Experimental Matrix**

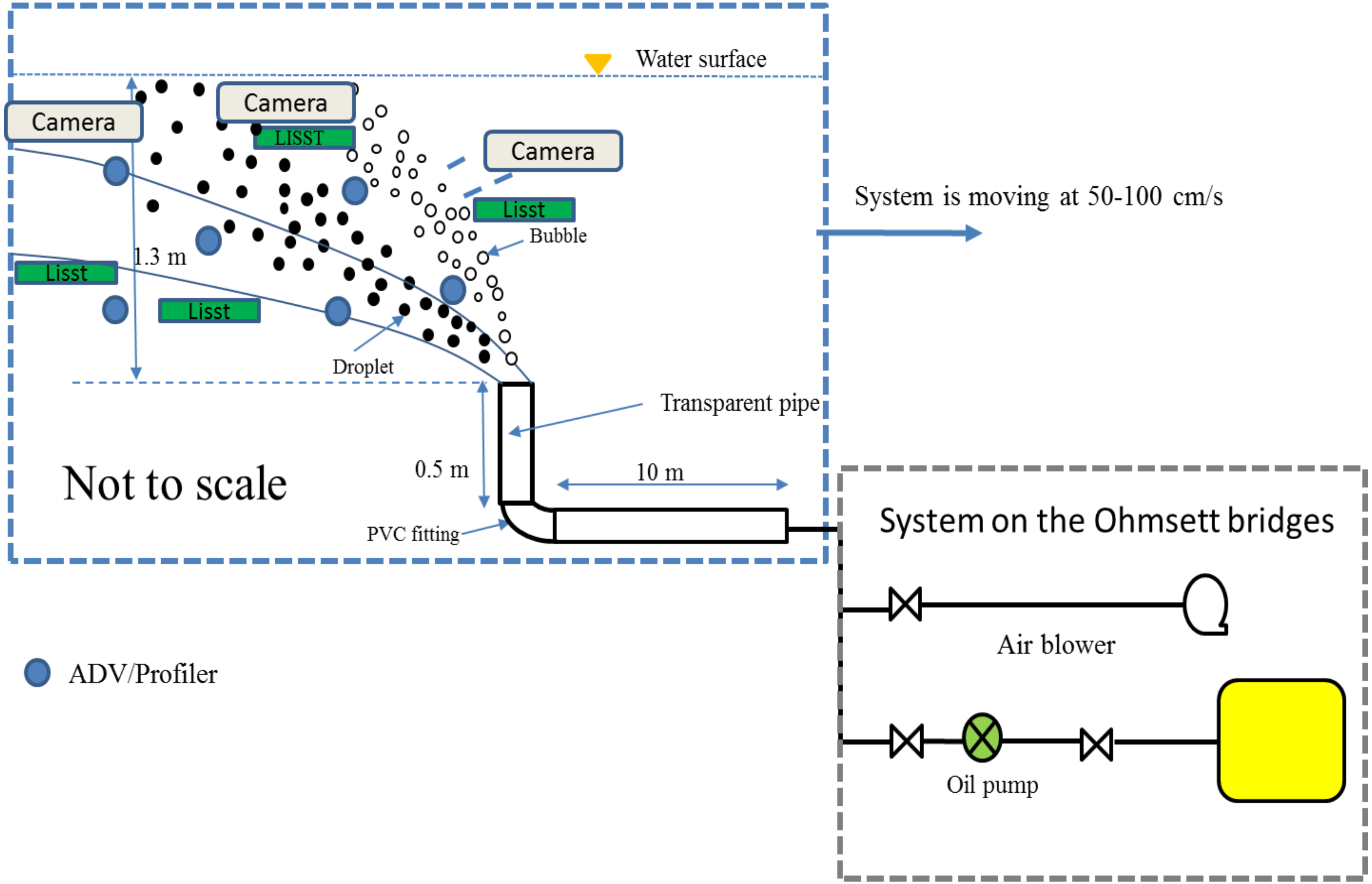
| Oil flow rate (L/min) | Air flow rate (L/min) | GOR |
|---|---|---|
| 40 | 0 | 0 |
| 40 | 180 | 4.5 (Churn flow) |
| 40 | 6 | 0.15 (bubbly flow) |
| 80 | 0 | 0 |
| 120 | 0 | 0 |
| 140 | 0 | 0 |

**Oil Properties**

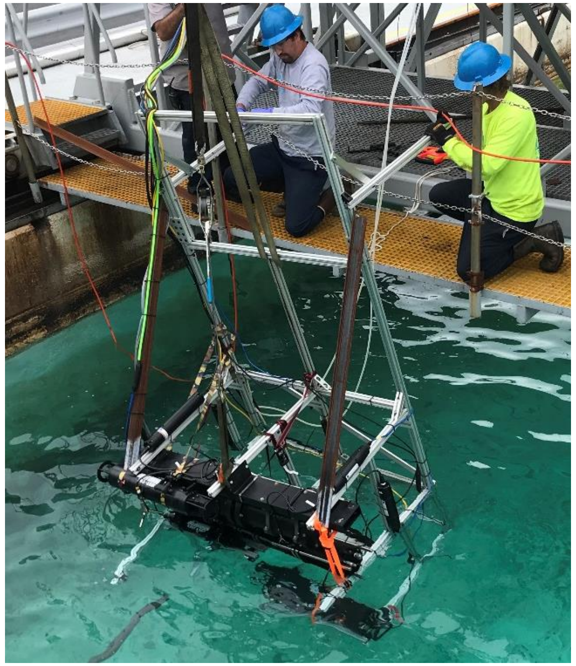
| Fuel oil #2 | |
|---|---|
| Density ($kg/m^3$) | 850 |
| Viscosity (cp) | 8.0 |
| Interfacial tension (mN/m) | 16.2 |

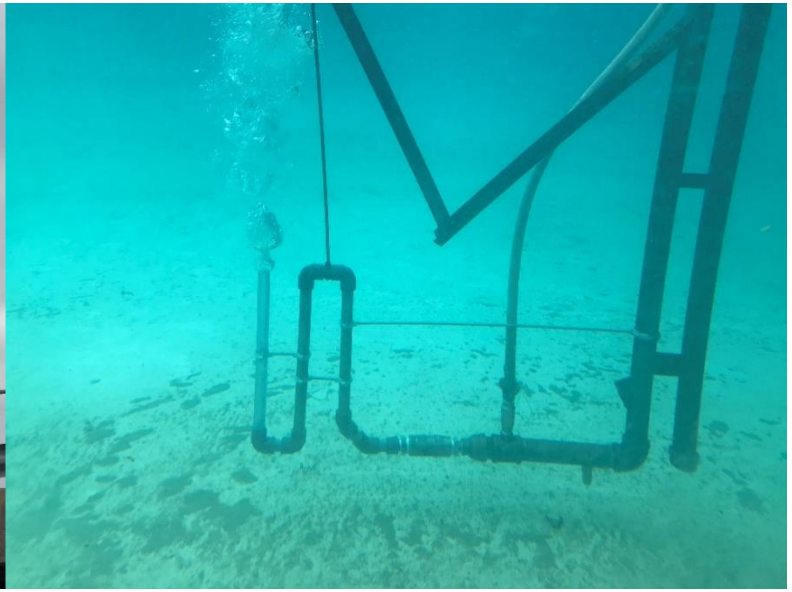
Project funded by CARTHE for June 2018

Blue dashed box is system in the Ohmsett tank

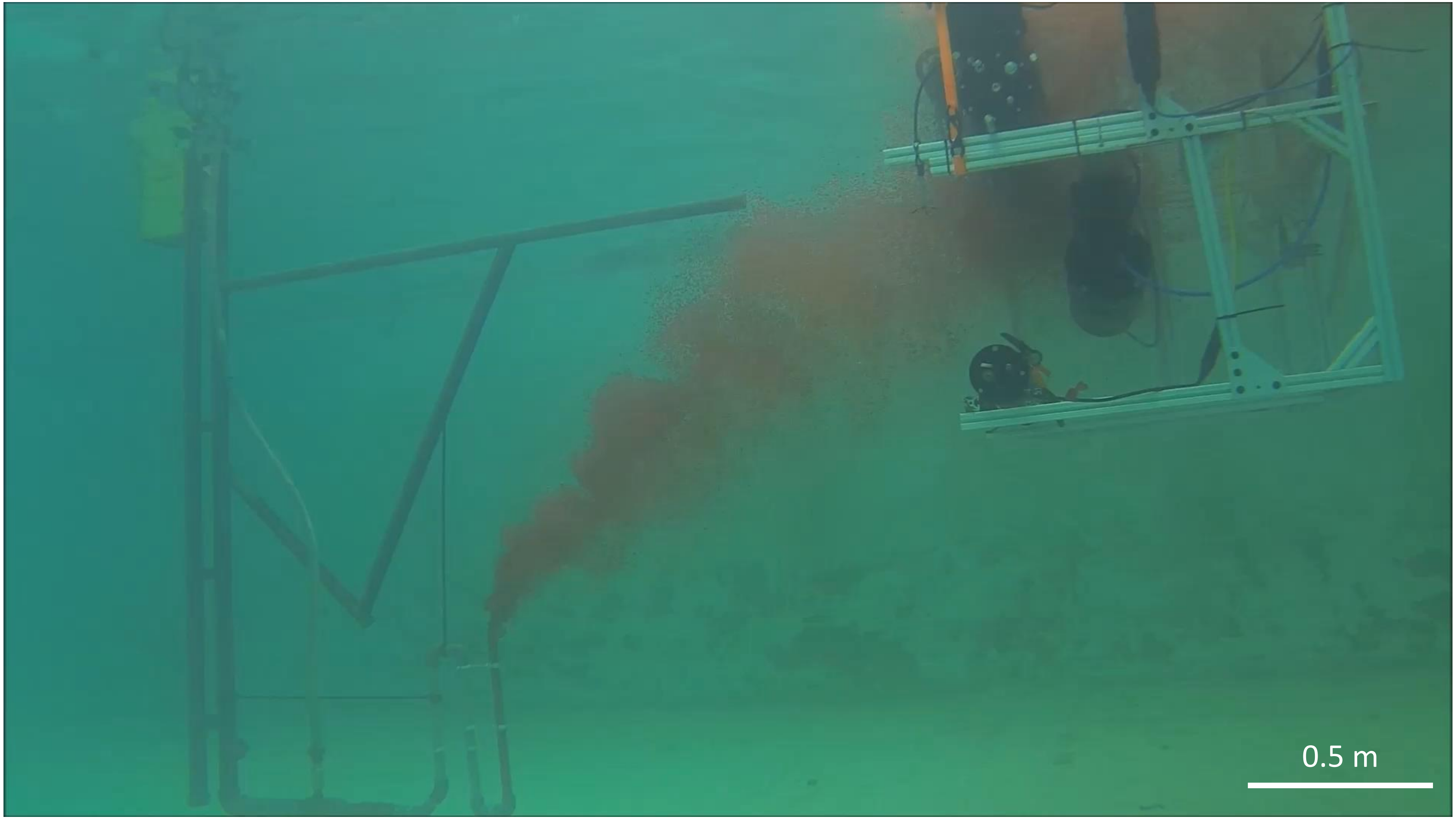



ADV/Profiler



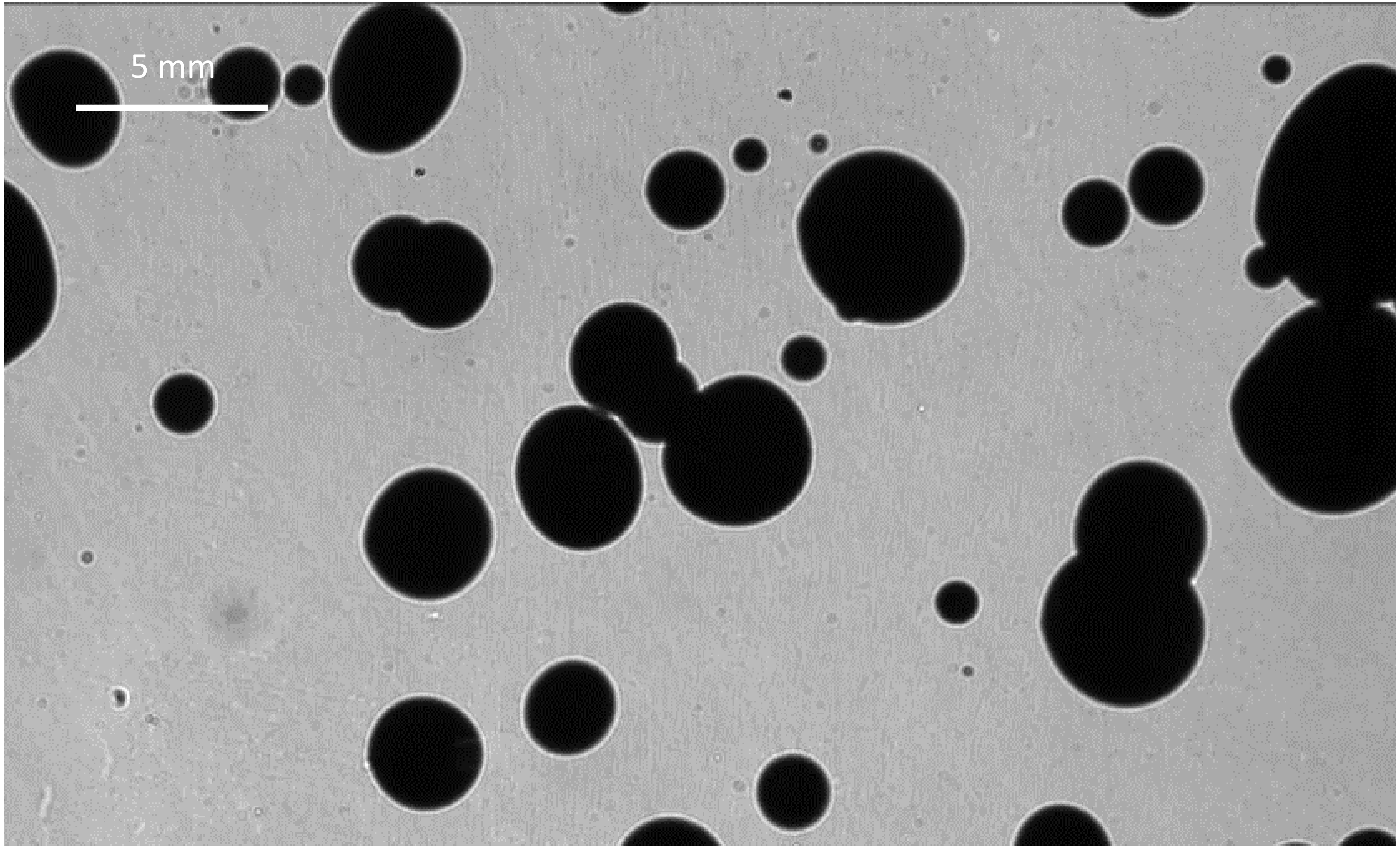


Oil only: $Q_{oil}$ = 40 L/min, No Air



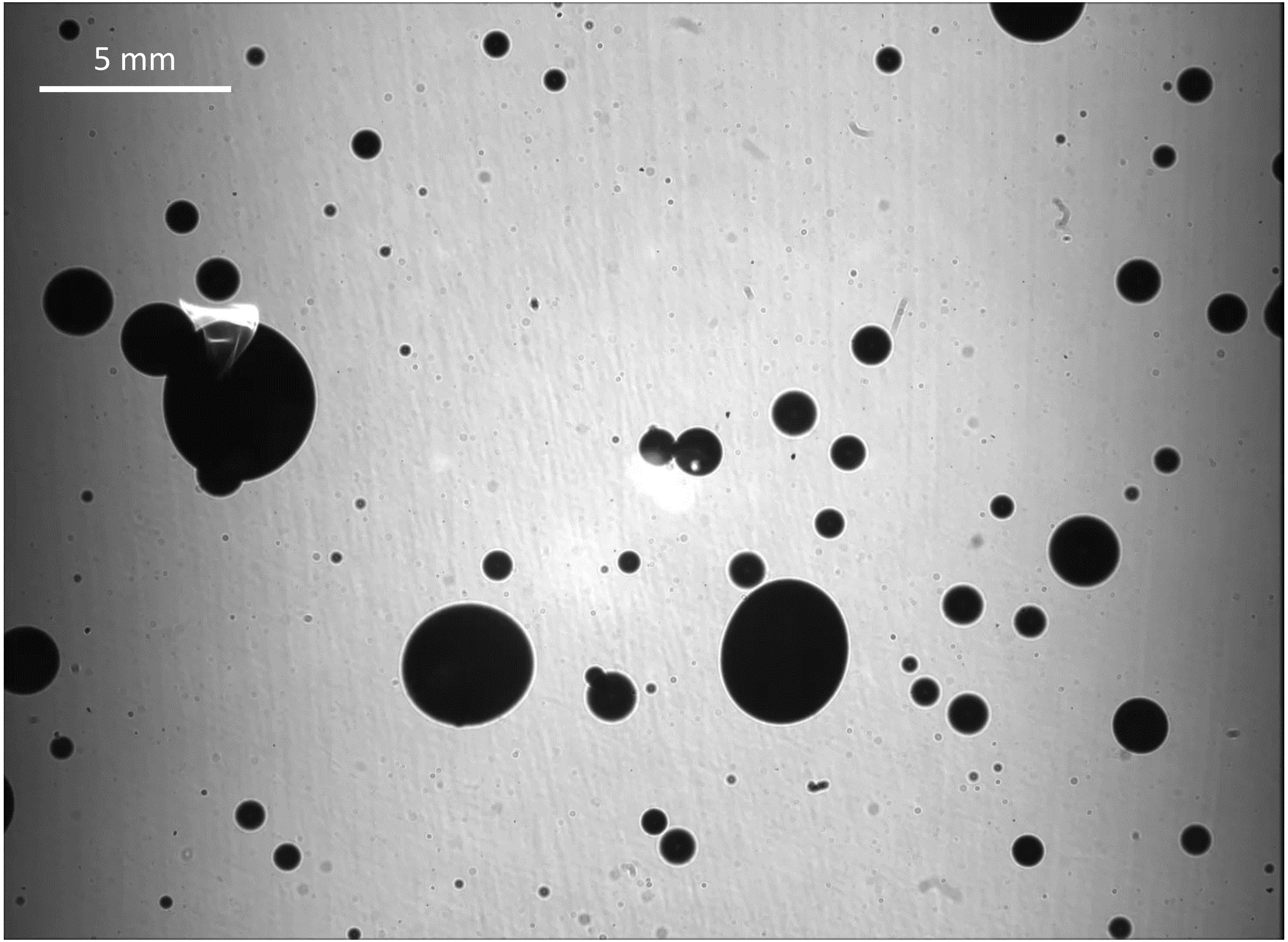
# Upper plume (top ShadowCam)

**Oil only: $Q_{oil}$ = 40 L/min, No Air**

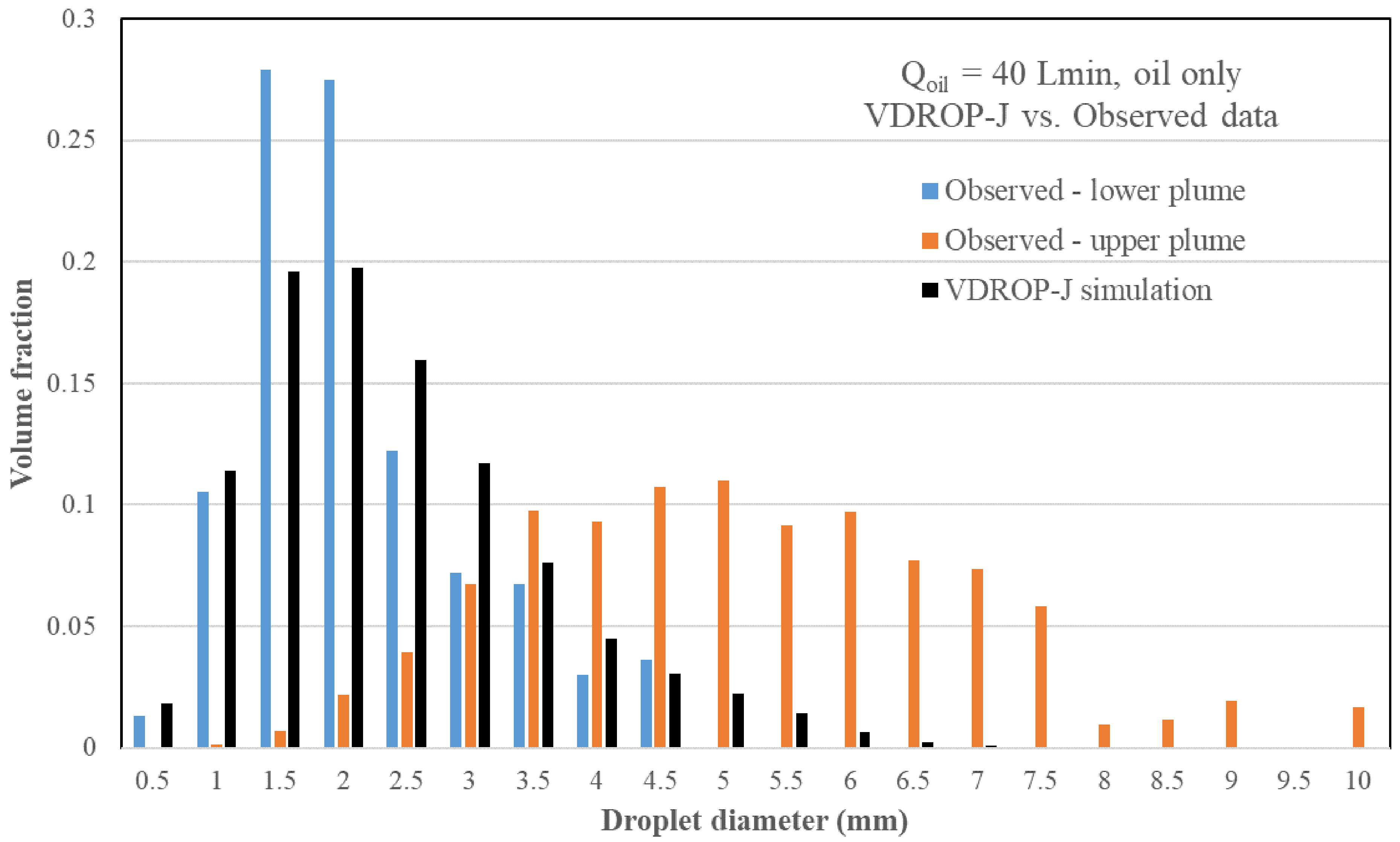


Oil only: $Q_{oil}$ = 40 L/min, No Air

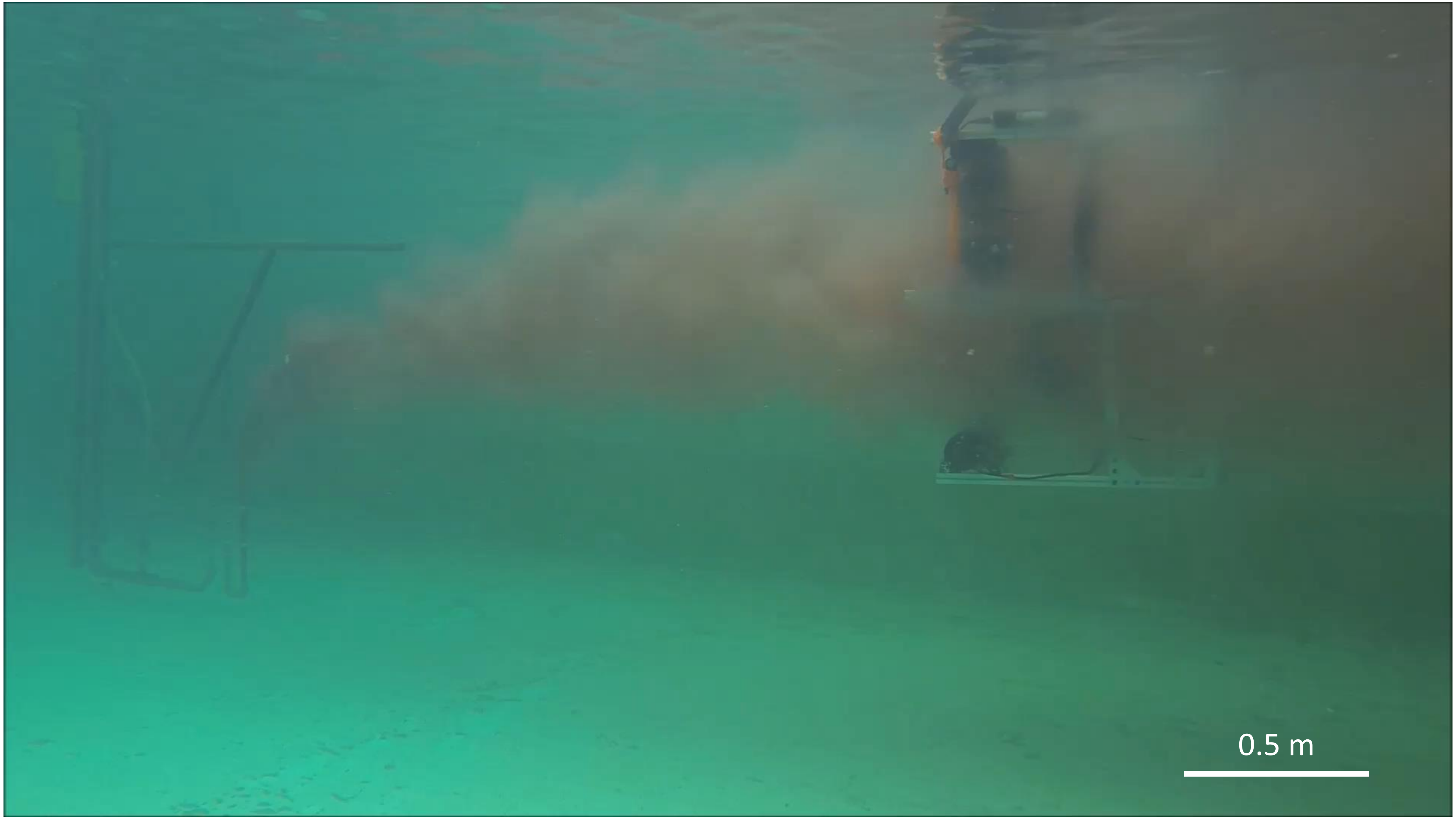
# Lower plume (bot ShadowCam)



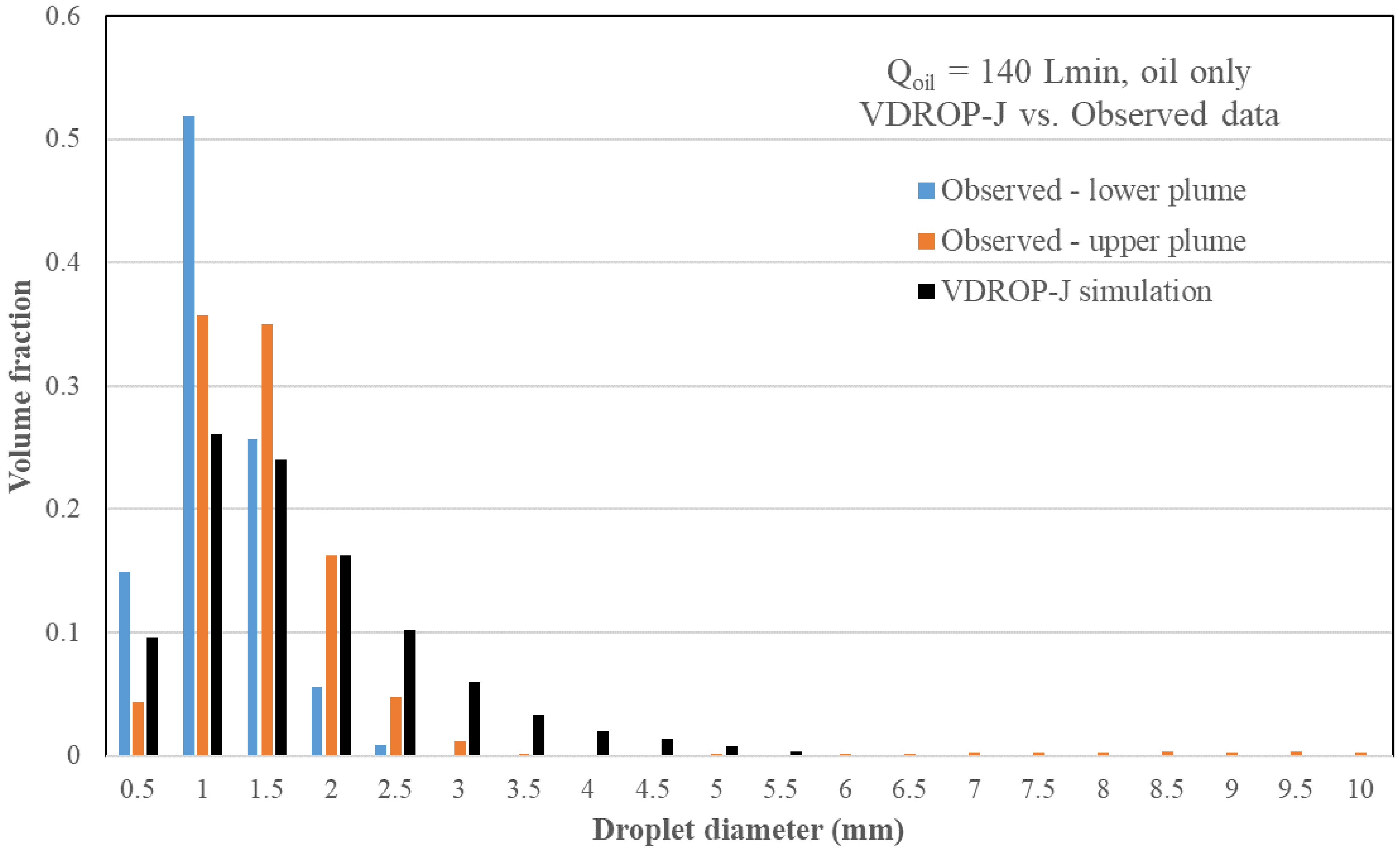
# VDROP-J simulation



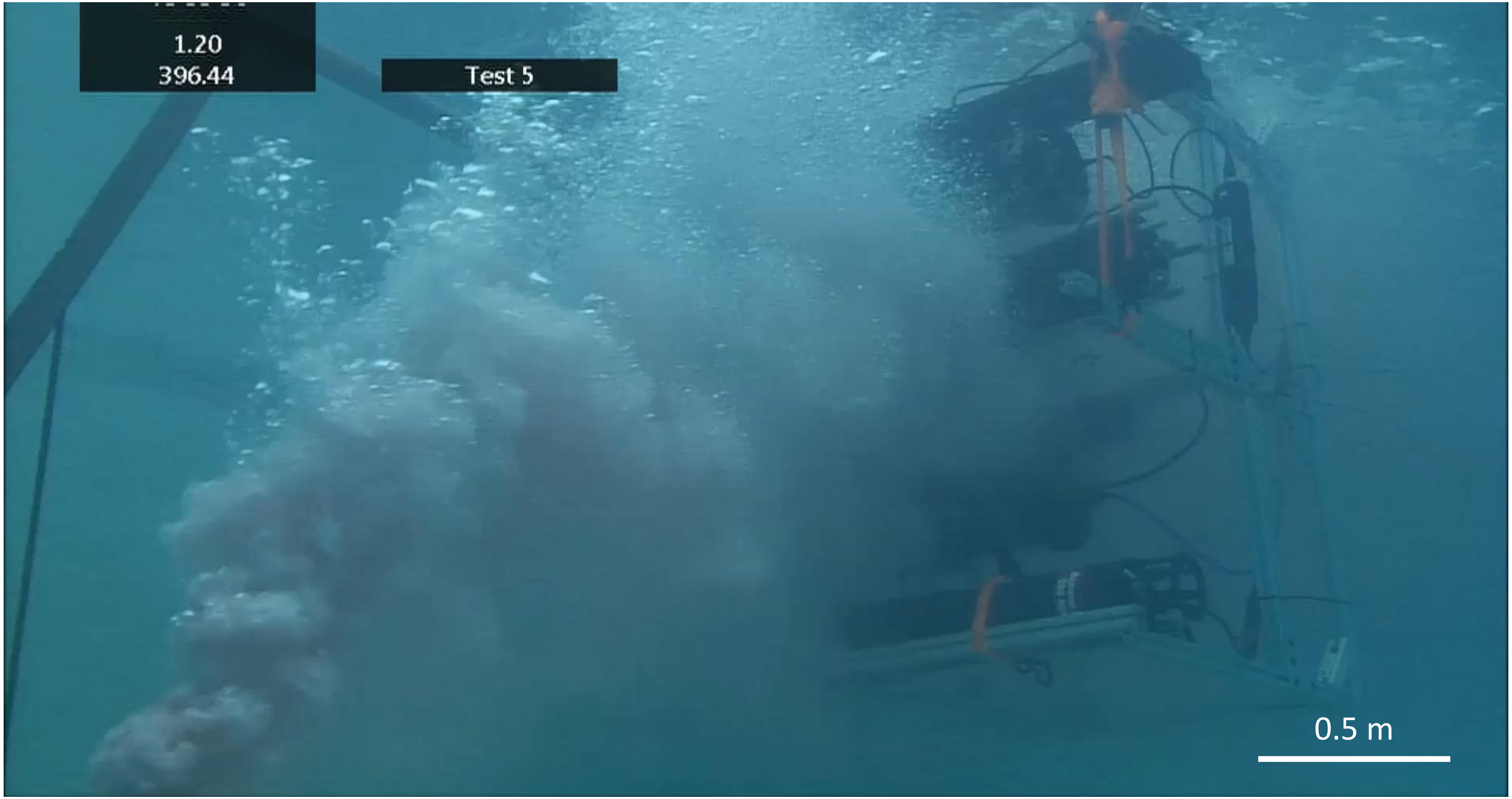
# Oil only: $Q_{oil}$ = 140 L/min, No Air



# VDROP-J simulation

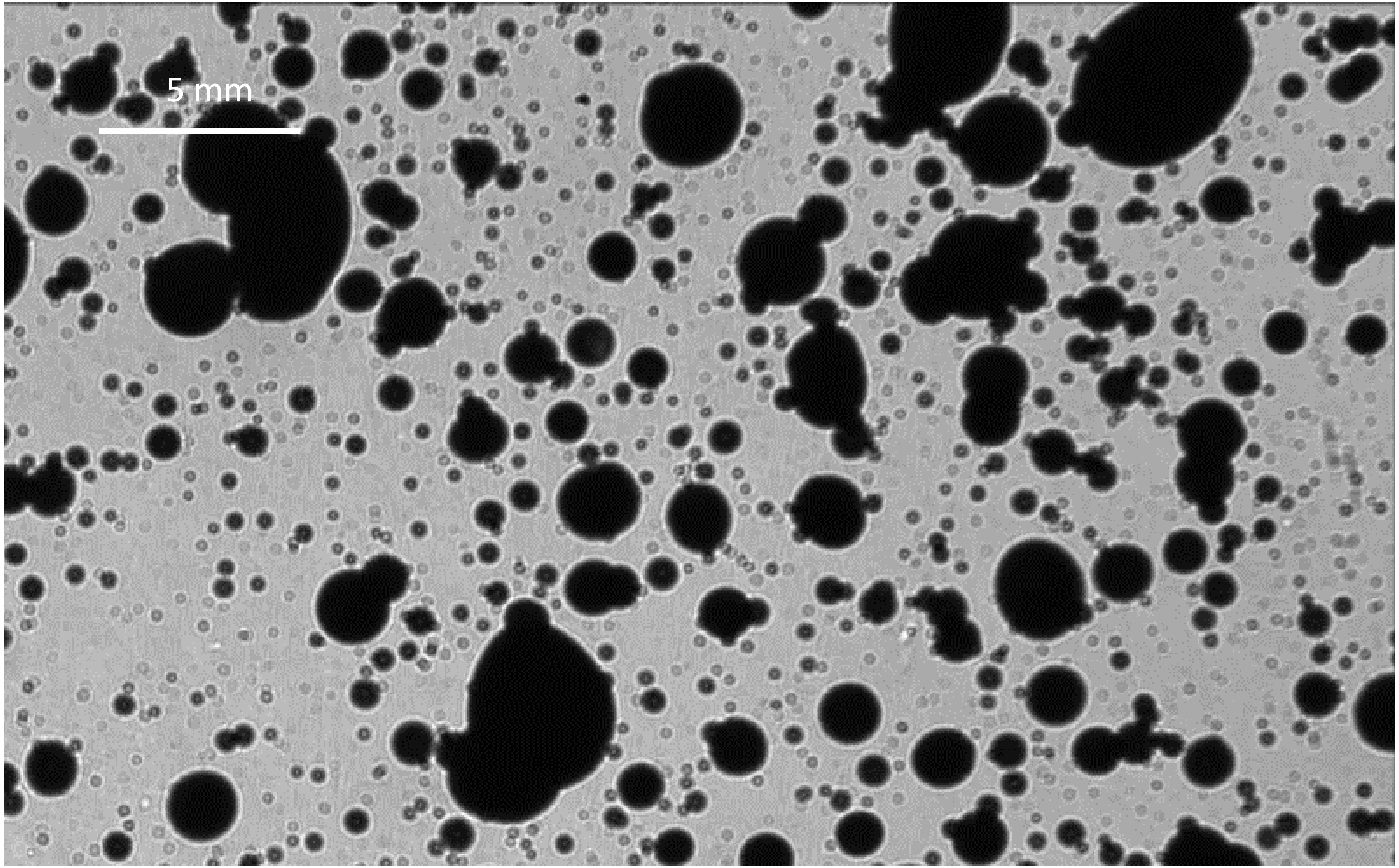


# Churn flow: $Q_{oil}$ = 40 L/min, $Q_{air}$ = 180 L/min



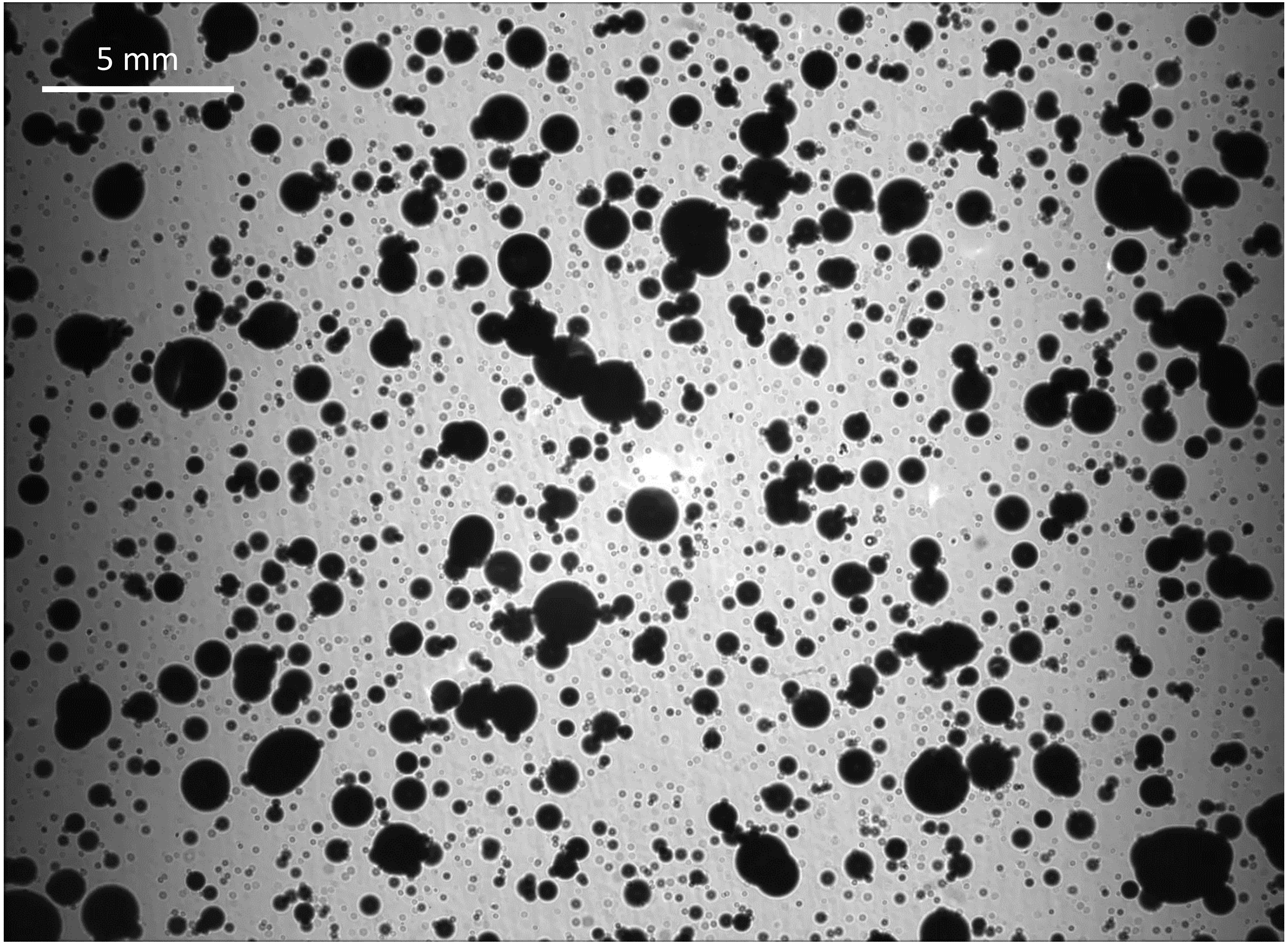
# Upper plume (top ShadowCam)

**Churn flow: $Q_{oil}$ = 40 L/min, $Q_{air}$ = 180 L/min**

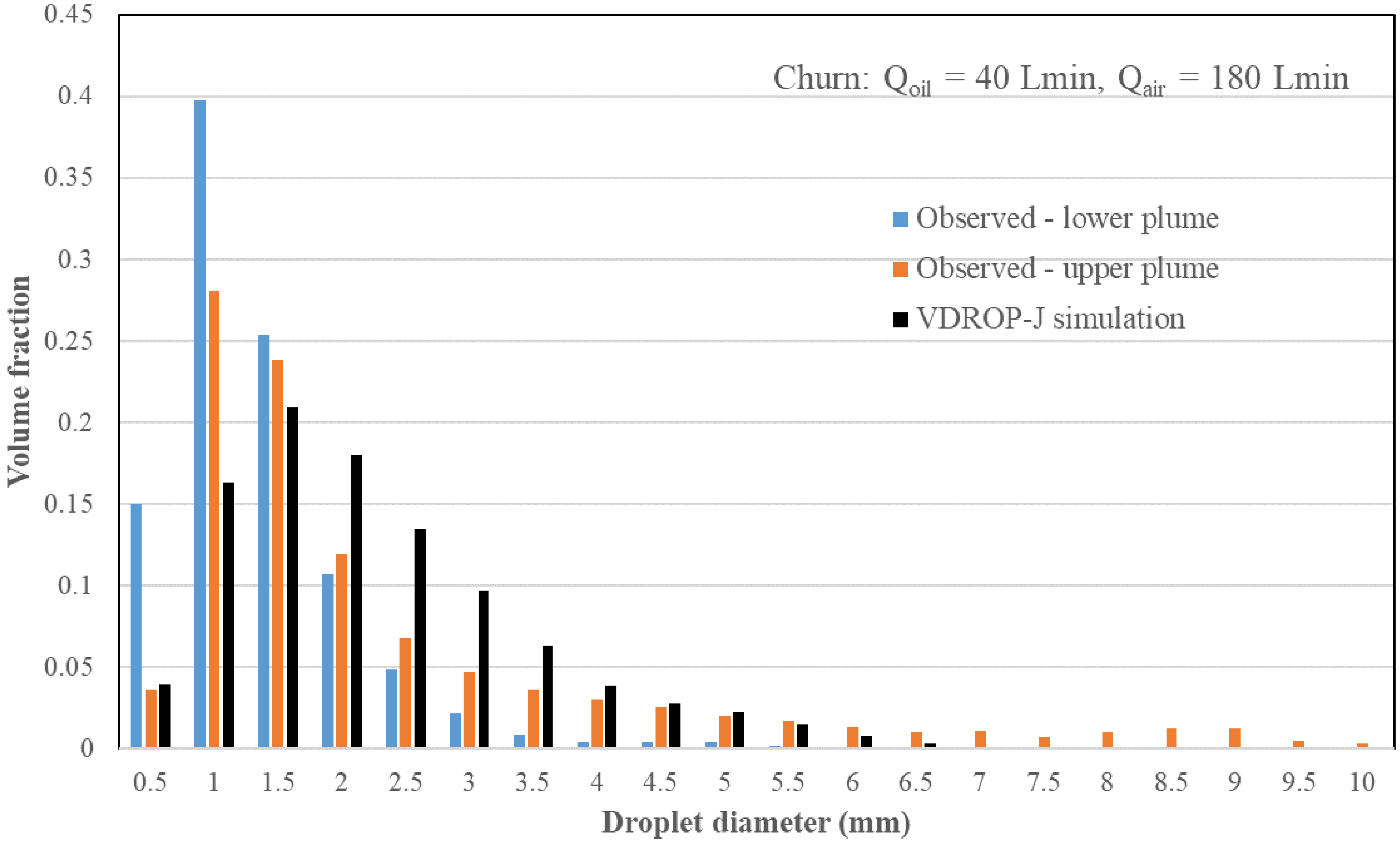


Churn flow: $Q_{oil}$ = 40 L/min, $Q_{air}$ = 180 L/min

Lower plume (bottom ShadowCam)



# VDROP-J simulation



# Conclusions

Segregation of the droplets within the horizontal plume.

Droplets at the top are larger (buoyancy).

Churn flow produced smaller droplets (as expected).

Future experiments would be with dispersant, funded by the Multi Partner Research Initiative (Kenneth Lee)