MEMORIAL UNIVERSITY

Multi Partner Oil Spill Research Initiative (MPRI)

MPRI Spill Treating Agents Project

Dispersant Field Trials in High-Energy Canadian Marine Environment

Michel Boufadel, Helen Zhang

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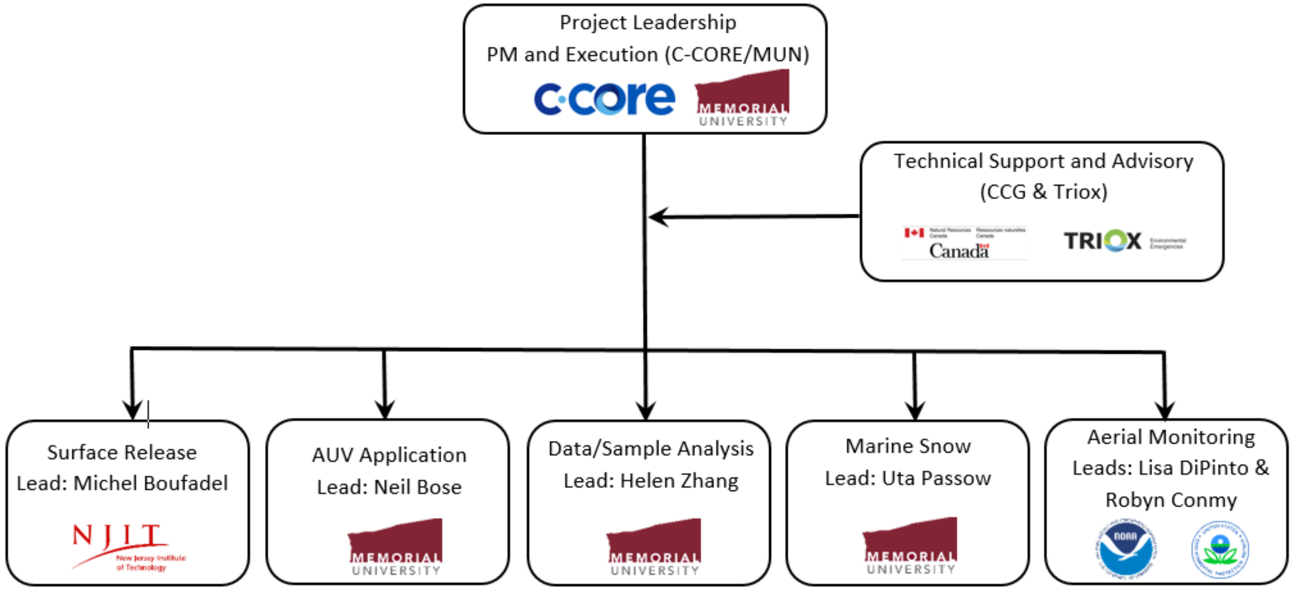
Key Project Objectives

- Better understand the performance of dispersants approved for use in Canada
- Develop and calibrate the predictive models for dispersant effectiveness
  - Support for operational decision making
- Helping to ensure Canada is prepared to effectively remediate a large spill/disaster
- Develop both HQP and the skillsets & experience for the end user



Co-PIs/Collaborators

Science Team

- Dr. Neil Bose: Principal Investigator (Memorial University)
  - VP Research at Memorial University – Prof. Maritime Hydrodynamics – AUVs for detection of oil at sea
- Dr. Michel Boufadel: Co-Principal Investigator (NJIT)
  - Prof. Civil & Environmental Engineering at NJIT & Director of Center for Natural Resources at NJIT
  - Exxon Valdez Spill (2007-2012), Deepwater Horizon Spill (2010), Enbridge Spill in Michigan (2010)
- Dr. Helen Zhang: Co-Principal Investigator (Memorial University)
  - Prof. Civil Engineering at Memorial & T2 Research Chair in Coastal and Environmental Engineering
  - Studies transport and fate of oil and emerging contaminants
- Dr. Uta Passow: Co-Principal Investigator (Memorial University)
  - Canada T1 Research Chair in Biological Oceanographic Processes
  - Studying oil/dispersant interaction with marine particles – do these harm organisms feeding on it
- Dr. Robyn Conmy: Co-Principal Investigator (US Environmental Protection Agency - EPA)
  - Oil Spill Response Research Area Lead at EPA & vice-chair of Interagency Coordinating Committee for Oil Pollution Research
  - Deepwater Horizon Spill – on response vessels, Unified Command, Federal Joint Analysis Group
- Dr. Lisa DiPinto: Co-Principal Investigator (National Oceanic & Atmospheric Administration - NOAA)
  - Senior Scientist for NOAA's Office of Response and Restoration
  - Chief Scientist for NOAA's Deepwater Horizon Natural Resource Damage Assessment

Project Motivation

- In order to effectively treat an oil spill – responders/decision makers need to be able to select most appropriate approach
    - Need a full “tool box” to select from
- Calm sea conditions: mechanical recovery is most appropriate
- Agitated seas: Mechanical recovery could pose risk to responders and might not be logistically possible. Dispersants are the only tool.
- Dispersants break the oil into small droplets that “disperse” into the water column. The droplets could subsequently biodegrade.
- Understanding dispersant behaviour becomes very important
    - When is it appropriate to use dispersant?
    - Needs to be a Net Environmental Benefit
- Data is lacking to effectively calibrate the models for dispersant behaviour
- Key technical components missing in models:
    - Oil droplet size distribution & variation with depth

Flask on an orbital shaker

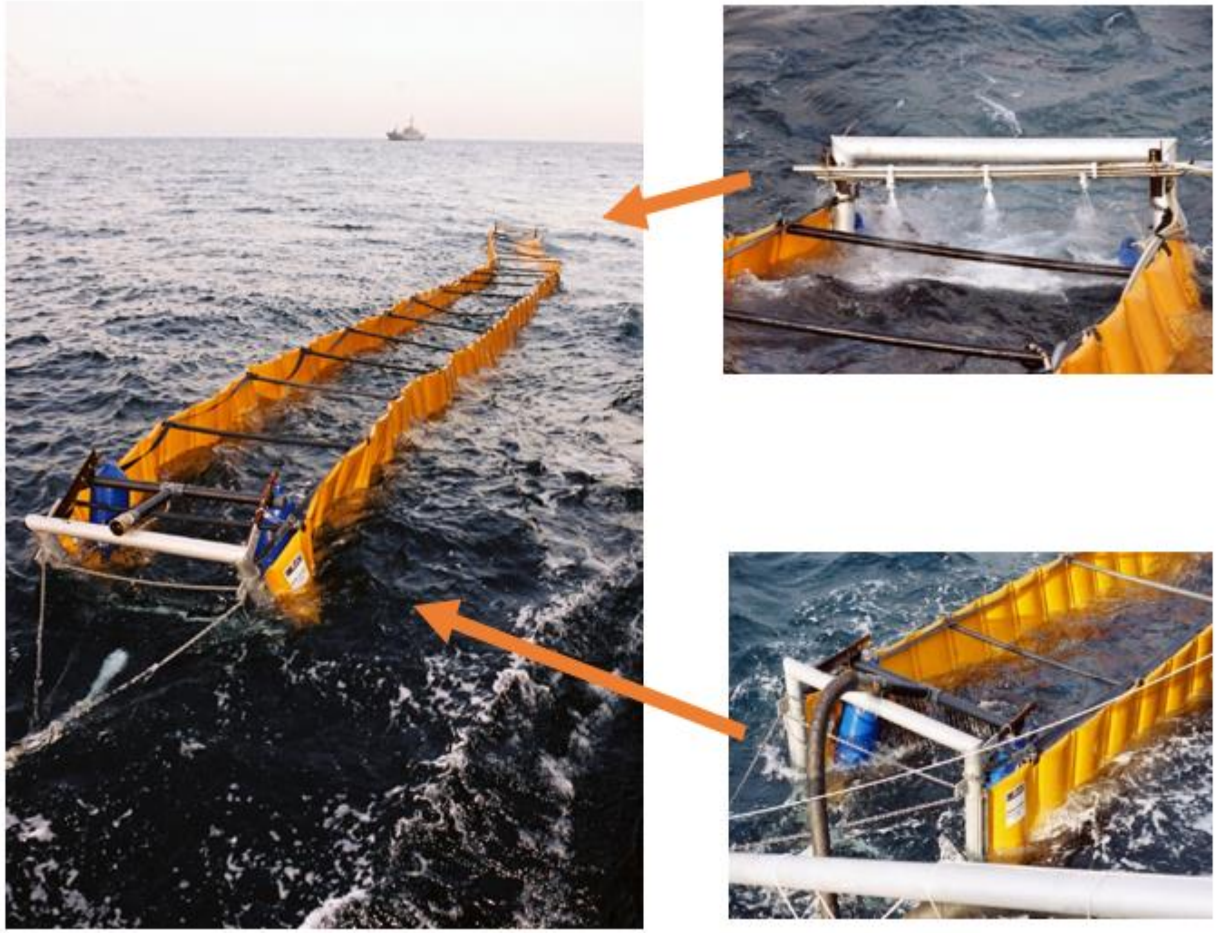
No Dispersant

With Dispersant 1:20

Why Field Studies?

- Lab & meso-scale experiments are often limited by the ability to capture the complexity of the field conditions
  - Closed environment – boundary effects
    - Limits oil spreading at surface & oil dilution/dispersion in the water column
  - Size alone is not sufficient, as dilution cannot occur without mixing.
  - The ocean contains mixing currents that emanated years and 100s of Kms away.
  - A tank can reproduce the behavior of oil at the water surface but not the 3D transport.
    - What effect does this have on the oil behaviour
    - Very challenging to replicate at the meso-scale
- Opportunity to combine novel methods for both *Aerial and Surface monitoring* so we can properly quantify the performance of dispersants

Surface Release of Oil & Dispersant



Lead by: Michel Boufadel (NJIT)

- Natural dispersion/entrainment vs effect of dispersants
- Oil droplet size & variation with depth
  - effect of dispersant
- Improvement and calibration of predictive models – requires and increased understanding of:
  - Oil spreading
  - Photooxidation
  - Dissolved oil and suspended droplets
  - Formation of MOSSFA

Surface Release Test Plan

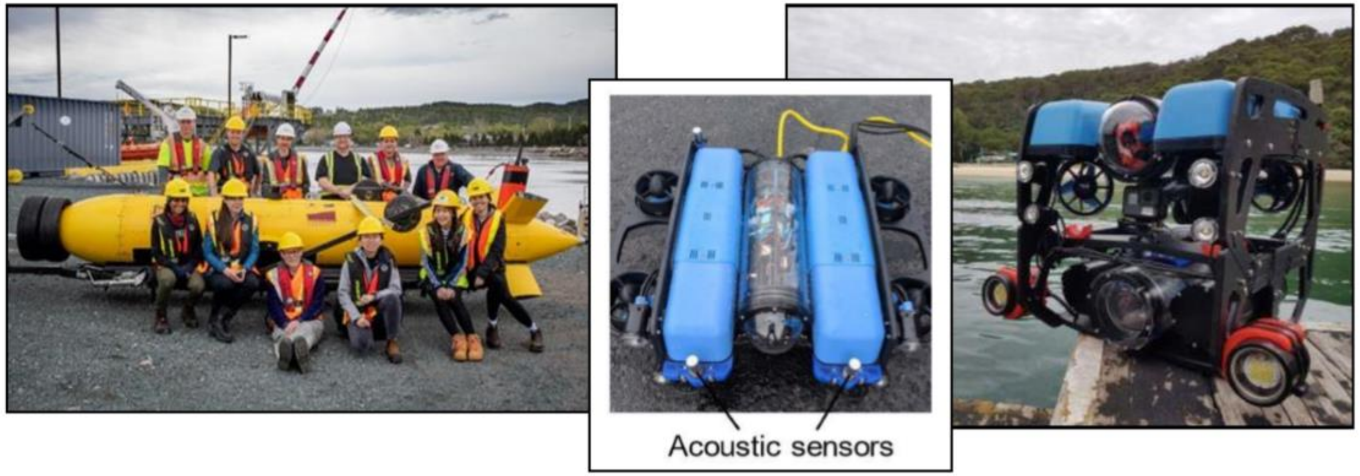
- Each test will release up to 1 m^3 (1000 L) of weathered oil
- Dispersant: Corexit 9500A (DOR of 1:20)
- Planning to conduct 12 releases + dye test
- Varying the degree to which the oil is weathered (5%, 10% loss of mass)
- Weathered oil subjected to photooxidation
- Conducting measurements and monitoring for up to 2 hours after the release

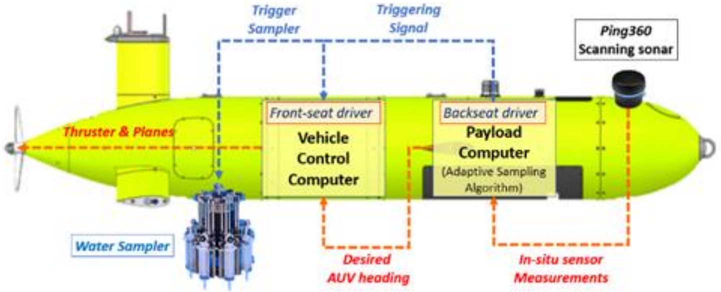
Oil#1=Weathered to 5% loss per mass, Oil#2= Weathered to 10% loss per mass. Oil#3: Weathered oil to 10%+photooxidation. Corexit9500A will be the dispersant.	
Exp1	Fluorescein Dye. Measurement for 3 hours.
Exp2	Repeat Exp1 (if possible)
Exp3	Oil#1. No dispersant. Measurement for 2 hours.
Exp4	Repeat Exp3 (if possible)
Exp5	Oil#2. No dispersant. Measurement for 2 hours.
Exp6	Repeat Exp 5 (if possible)
Exp7	Oil#3. No dispersant. Measurement for 2 hours.
Exp8	Repeat Exp7 (if possible)
Exp9	Oil#1. WITH dispersant. DOR 1:20. Measurement for up to 1 hours.
Exp10	Repeat Exp9
Exp11	Oil#2. WITH dispersant. DOR 1:20. Measurement for up to 1 hours.
Exp12	Repeat Exp11
Exp13	Oil#3. WITH dispersant. DOR 1:20. Measurement for up to 1 hours.
Exp14	Repeat Exp13

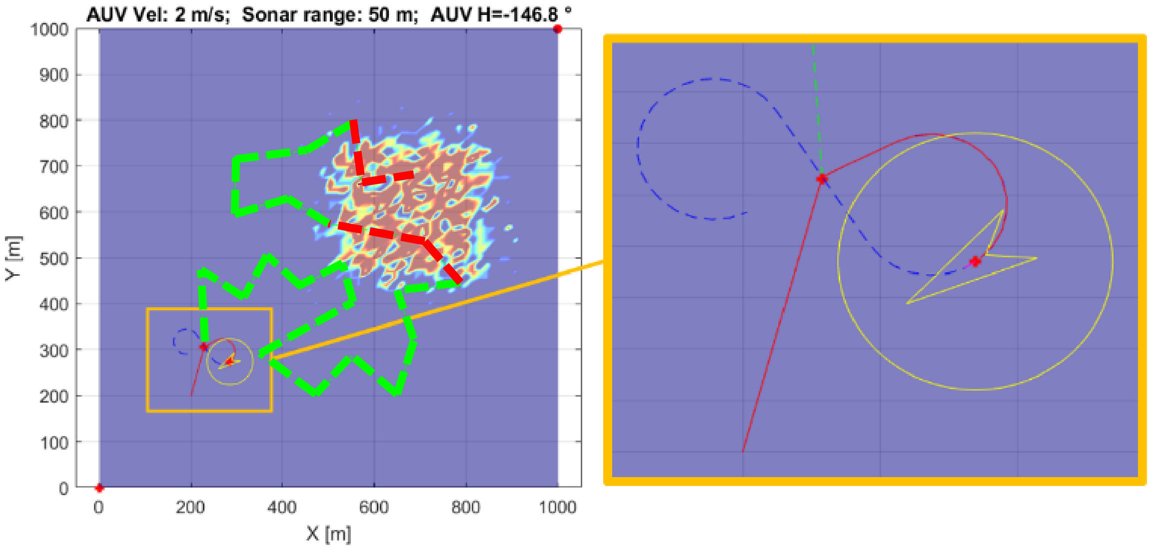
Data Collection

- Data:
  - Acoustic sonar
  - Fluorometry on ROV
  - LISST, shadowgraph, holographic cameras
  - Water samples
- Metocean data
  - Currents, waves, and water velocity
  - Temperature and salinity (buoyancy gradients)
- AUV Path (vel. 2 m/s)
  - Detect – Delineate – Sample

Lead by: Neil Bose (Memorial)



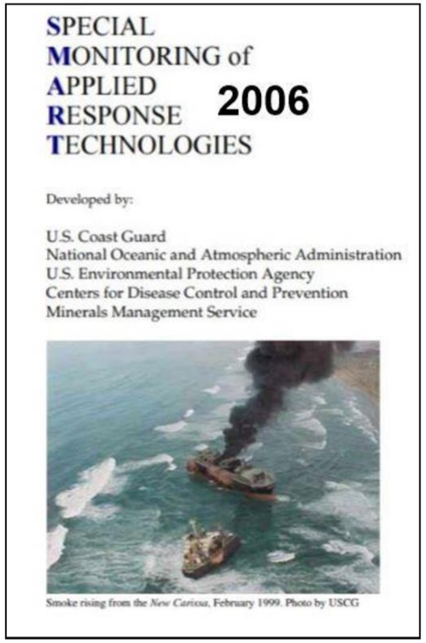


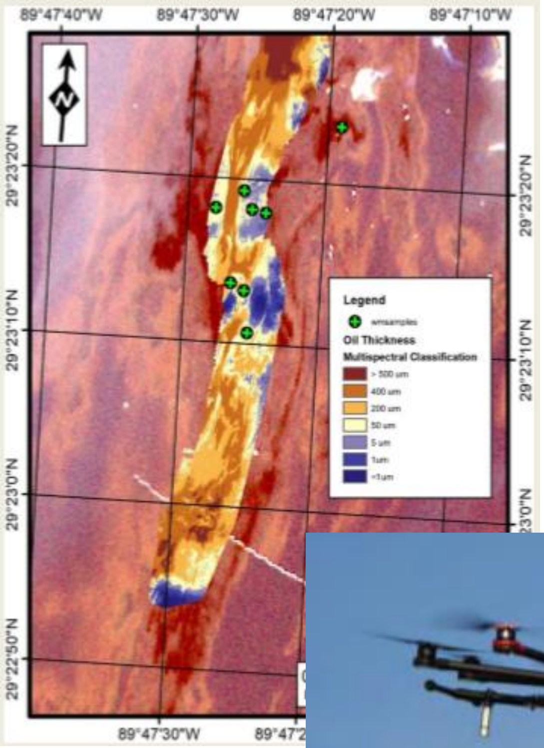


Aerial Data Collection & SMART Protocols

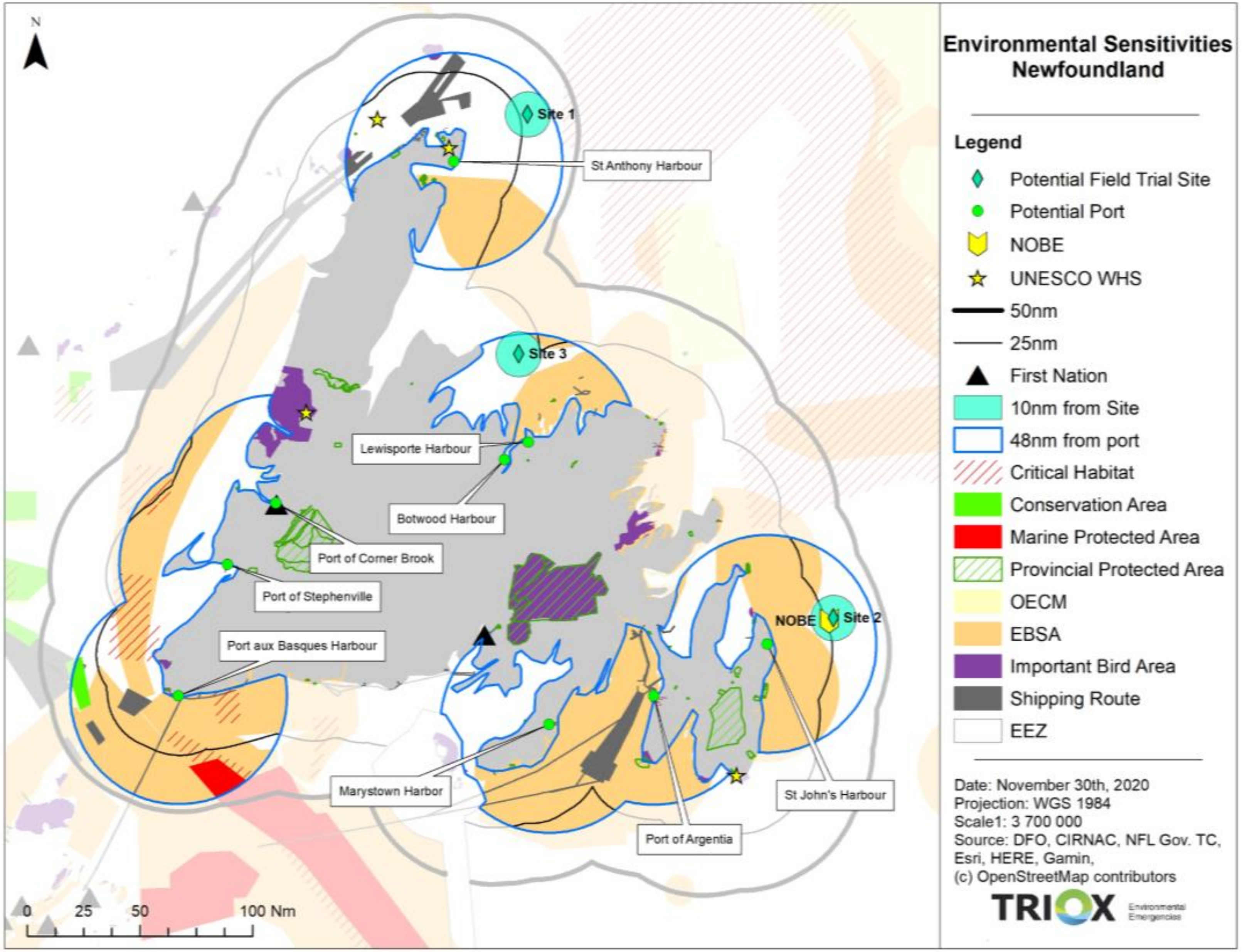
Lead by: Lisa Dipinto (NOAA), Dana Tulis (USCG), Robyn Conmy (EPA)

- Updating protocols for conducting dispersant monitoring programs (SMART)
- Drones/UAV – multispectral sensors
  - Observing what oil looks like before and after dispersant application
  - Surface oil mapping
- Satellite detection & monitoring – surface oil mapping
- ROV for subsea monitoring
  - Fluorometer, CTD & water sampling
  - Water column concentrations and dispersion
- Drifter buoy
  - Oil displacement and dispersion
  - Miniaturized LISST – oil droplet size distribution





Planned Site Location



CCG

Preparedness and Mitigation Measures

Contingency Plans under development (additional plans will be developed ie. Medical, Surveillance, Security, Fuel management, etc.)

- Safety Plan
- Oil Spill Response Plan
- Wildlife Response Plan
- Decontamination Plan
- Waste Management Plan
- Communications Plan

Chemical Data Collection

A comprehensive evaluation of early mass transfer of the spilled oil with/without the application of dispersants in surface/subsea field testing

- **Temporal and spatial distribution** of saturates, aromatics, resins, and asphaltenes during the field trial

- **The contribution of** evaporation, dissolution, and photooxidation to and verification of oil early mass transfer mechanisms

Memorial facilities for sampling and oil characterization

GC-MS/MS (Saturate/aromatics/resin)

FT-ICR/MS(Resin/asphaltene)

AUV (Memorial)

^1H NMR (SARS)

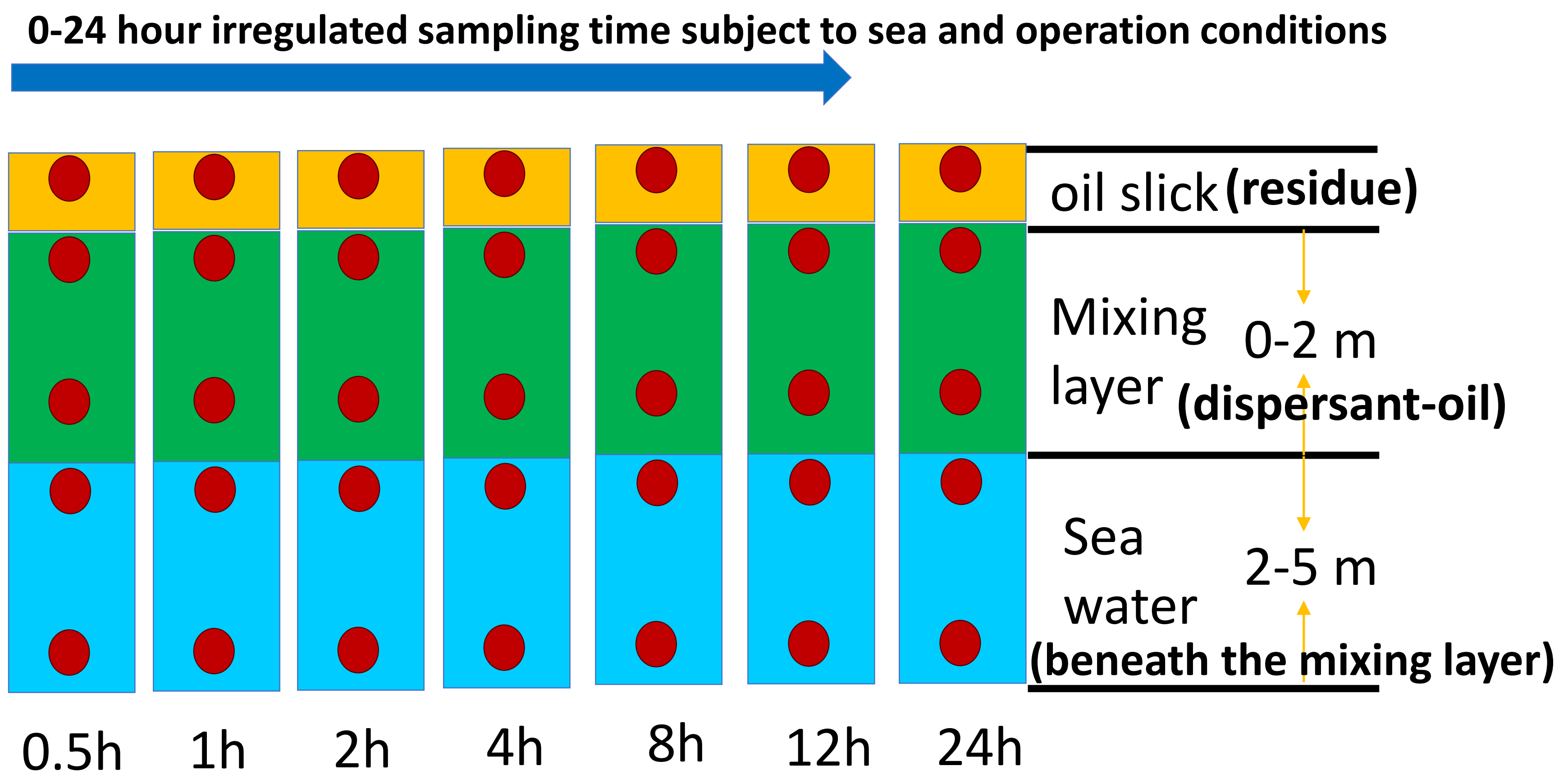
GC-FID (TPH)

TLC-FID (Oxygenated hydrocarbons)

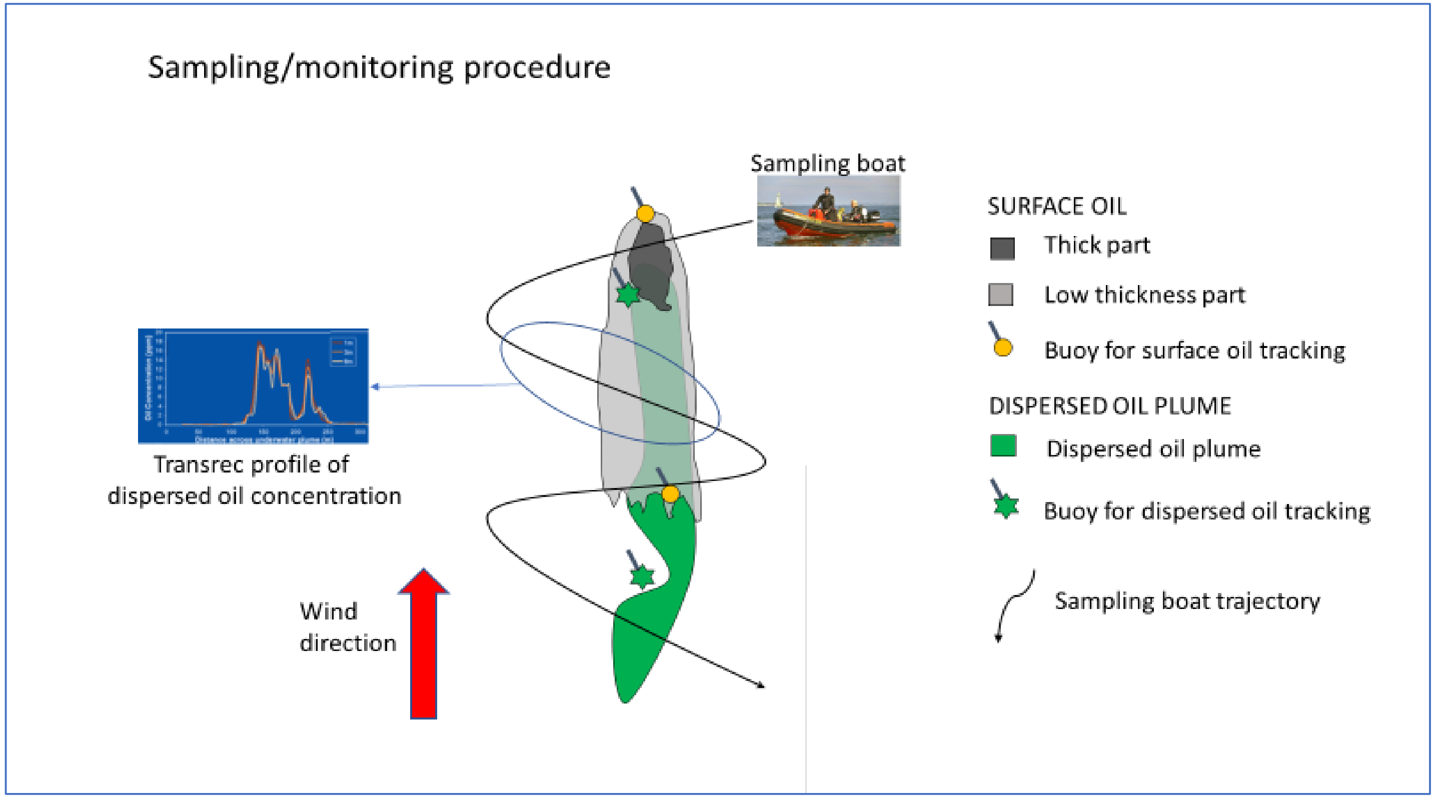
FT-IR (SARS)

ICP/MS (Seawater matrix)

Sampling plan for surface dispersant injection

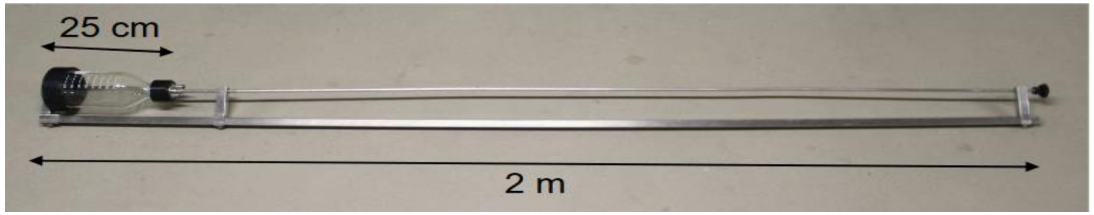


Surface sample collection (from the sampling boat)



Boats will follow the buoy tracking the oil plume.

- Example sampler



Subsurface sample collection (AUV/ROV)

Sampling via autonomous underwater vehicle (AUV)

Sampling via remotely operated vehicle (ROV)

Samples Transportation and Storage

- Samples from oil slick/water column will be preserved by the addition of 5-30mL of dichloromethane within 30 min after collection.
- Samples will be refrigerated (-20 ^{o}C) in the dark until the analysis in NRPOP.

Information to be obtained in the field trail

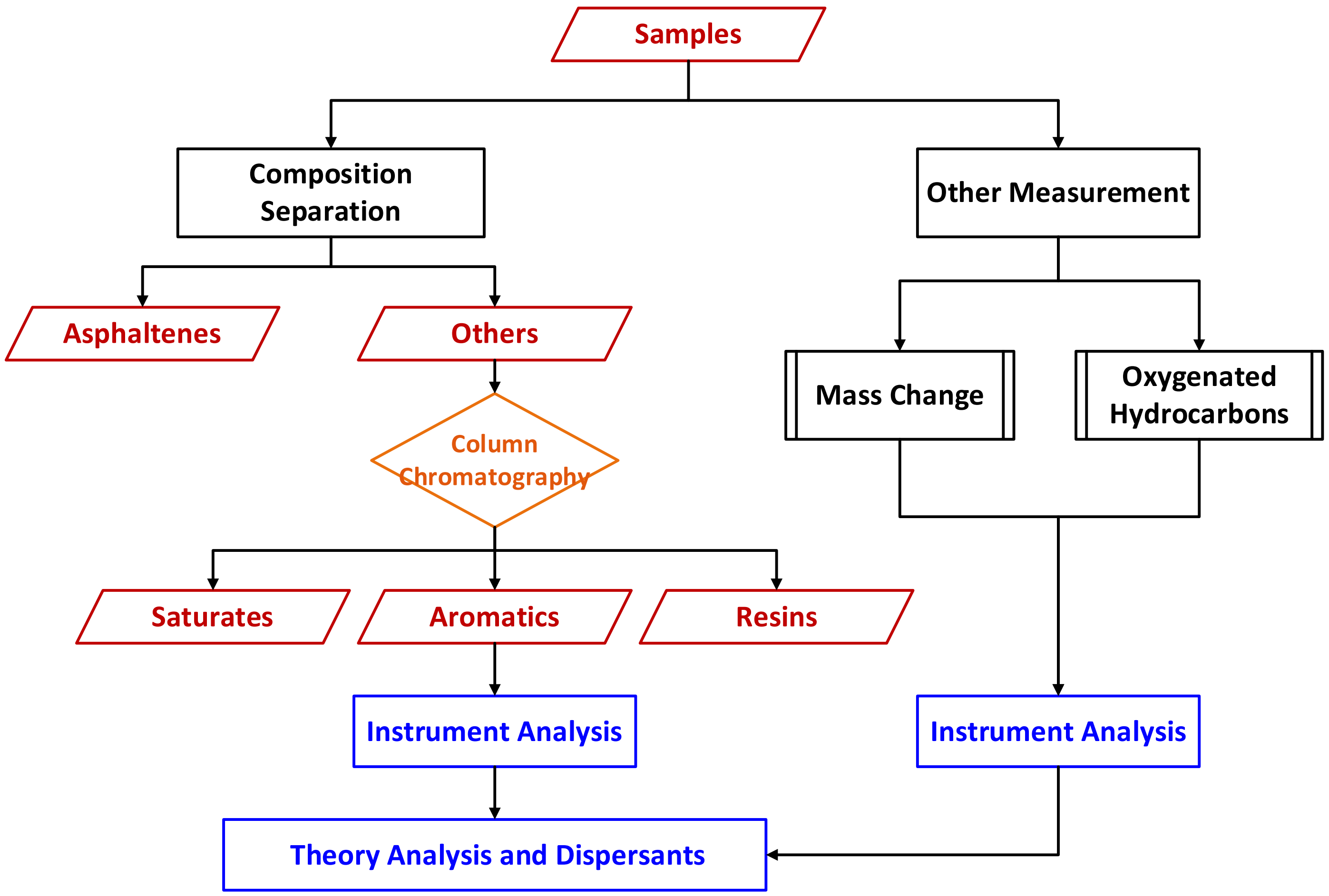
- Oil properties

- Position of oil slick/oil plume (latitude, longitude)
- Dimensions of oil slick/oil plume (depth, length, and width)
- Dimensions of the mixing layers (depth, length, and width)

- Environmental conditions

- Wind (speed/direction)
- Temperature (air/water at depths)
- Humidity
- Sunlight intensity (solar spectra/wavelength of sunlight)
- Wave conditions (radial and tangential velocity; turbulent velocity)

Lab oil composition analysis



- **Tracking temporal and spatial distribution** of saturates, aromatics, resins, and asphaltenes during the field trial

Lab biomarker analysis

- Fingerprinting strategy (with selected diagnostic ratios)
  - **Evaporation**
    - e.g.,$(\Sigma C_8\text{-}C_{14})/(\Sigma C_{22}\text{-}C_{28})$ $(\Sigma C_{10}\text{-}C_{25})/(\Sigma C_{17}\text{-}C_{25})$
  - **Dissolution**
    - e.g., Relative distribution of alkyl-PAHs
  - **Photo-oxidation**
    - e.g., 9/4-methyl-phenanthrenes/methyl-anthracene
- Concentration measurement

- **Tracking** evaporation, dissolution, and photooxidation during and right after field trail

Early mass transfer analysis

- Evaluating early mass transfer of spilled oil before/after the application of dispersants in surface/subsea field testing via empirical theories

$$F_{i,oil}|_{evap} = -\frac{C_{i,oil}}{\frac{\delta_{oil}}{D_{i,oil}} + \frac{\delta_{air}}{D_{i,air} \cdot K_{i,a/o}}} \qquad F_{i,oil}|_{diss} = -\frac{\frac{C_{i,water}}{K_{i,a/o}} - C_{i,oil}}{\frac{\delta_{oil}}{D_{i,oil}} + \frac{\delta_{air}}{D_{i,air} \cdot K_{i,a/o}}}$$

C is the concentration of a specific oil component
(C_{oil} = concentration in the oil layer; C_{water} = concentration in the water layer)
δ is the film thickness of a phase
(δ_{air} = air boundary film thickness; δ_{water} = water boundary film thickness)
D is the diffusion coefficient of an oil component in the indicated phase
K is the coefficient of an oil component between two phases
F is oil mass transfer flux due to a specific process

Thank you!