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Canada

An Update on Environment and Climate Change Canada's Oil Spill Research Activities

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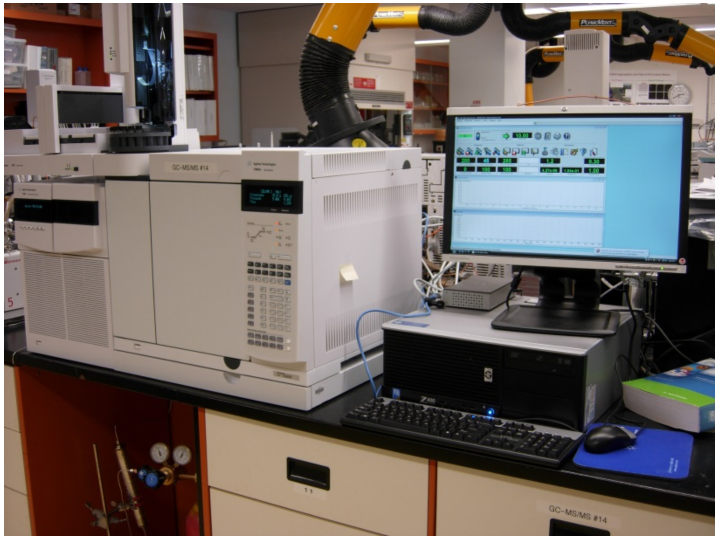
OSPR/Chevron Oil Spill Response
Technology Workshop
Chevron Park, San Ramon, CA

Fate and Behaviour of Oil Sands Diluted Bitumen

- Physical and chemical properties measurement of fresh and artificially weathered diluted bitumen products
  - 8 diluted bitumen products (dilbits and synbits) have been evaluated previously (2013-2015)
  - Recent studies have included 1 additional “neat” bitumen product (Bitumen 3126), Marine safe lube oil, and some conventional heavy crude oils for comparison.
- Continued fate and behaviour studies on weathering of dilbit (evaporation, emulsification, photo-oxidation etc.)

Fate and Behaviour of Oil Sands Diluted Bitumen

- Effect of evaporative weathering and oil-sediment interactions on the fate and behavior of diluted bitumen in marine environments evaluated.
- Physicochemical data and fate and behaviour information is essential for better predictive modelling of spilled petroleum.



Fate and Behaviour of Oil Sands Diluted Bitumen

- Analytical method development
  - Development of a rapid analytical method for petroleum characterization based on fluorescence spectroscopy.
    - Faster, simpler than GC methods
  - Validation of submersible fluorometer analytical response with gas chromatography and benchtop fluorescence spectrometer.
  - Development of an analytical method for trace heavy metals in different petroleum products (microwave acid digest method coupled with ICP-MS).

- A study was undertaken to evaluate the fluorescence response of resin and asphaltene fractions of petroleum samples.

Fate and Behaviour of Oil Sands Diluted Bitumen

- Studies were initiated at spills of opportunity (Environmental Emergency incidents) to enhance knowledge of the fate and behaviour of spilled petroleum products in the real world.
  - Freshwater – pipeline and train incidents
  - Marine – vessel incidents

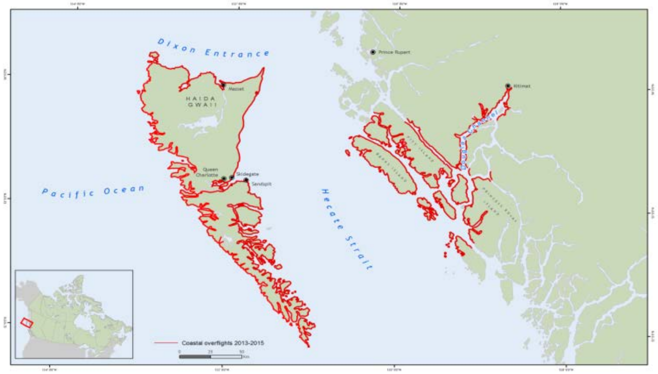
- Weathering studies and physiochemical property measurements for a number of light refined, crude and heavy oils.

Marine Shoreline and Related Field Studies – Unconventional Oil Spill R&D Program

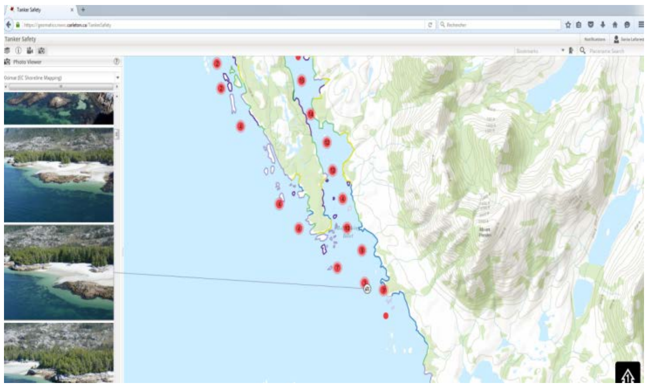
- Objectives
  - study the fate and behaviour and cleanup of unconventional crude oil (diluted bitumen) on marine shorelines under various conditions
  - deliver operational guidance and scientific information that is legally defensible and credible to spill responders for shoreline treatment option decisions
- Overview of the Studies
  - To support Area Response Planning
  - Five priority areas are:
    - Northwest BC coastline (Douglas & Grenville Channels and Haida Gwaii)
    - Southern British Columbia (Straits of Georgia and Juan de Fuca)
    - St. Lawrence: Montreal to Anticosti Island (Quebec)
    - Port Hawkesbury and the Strait of Canso (Nova Scotia)
    - Saint John and the Bay of Fundy (New Brunswick)
  - Literature review of the impacts of bitumen and fuels on marine shorelines
  - Develop and validate standardized on-site and laboratory methods to aid spill response decision-makers
    - detection and monitoring of spilled oil in the marine environment, improved understanding of oil fate and behavior, assess the short and longer term environmental impacts
  - Review and update ECCC H&S training and personal protective equipment protocols with the unconventional products

Marine Shoreline Diluted Bitumen Oil Spill R&D Studies:

- Approach
  - To address knowledge gaps for Area Response Planning
    - Aerial shoreline surveys - Douglas & Grenville Channels and Haida Gwaii in 2013-2015
    - Shoreline classification, with ground survey validation and sediment collection for subsequent baseline physical and chemical analysis
    - Baseline environmental data set will be available in hardcopy & electronic (GIS) to aid oil spill planning and response activities
    - Chedabucto Bay, Bay of Fundy and St. Lawrence shoreline surveys carried out in 2016
    - Laboratory and mid-scale oil-in-sediment penetration and adhesion studies
    - Studies to support the development of field SOPs to detect and quantify oil in the nearshore water/sediment and on/in the shoreline to support decision-makers
    - Field guide and job aid:
      - ECCC SCAT Manual, 3rd edition, in 2017
      - ECCC A Field Guide to Oil Spill Response on Marine Shorelines available at http://publications.gc.ca



Aerial survey conducted from 2013 to 2015



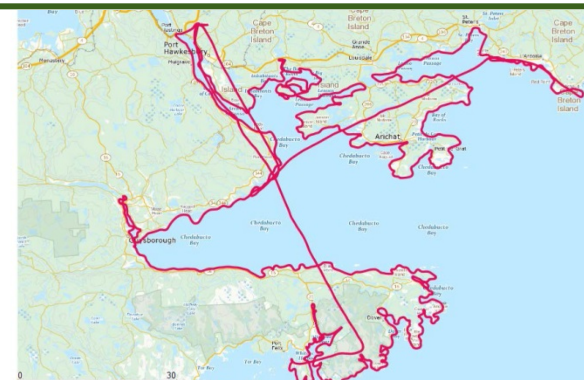
Screenshot of the ESTS web mapping application including pictures and segmentation of the shoreline

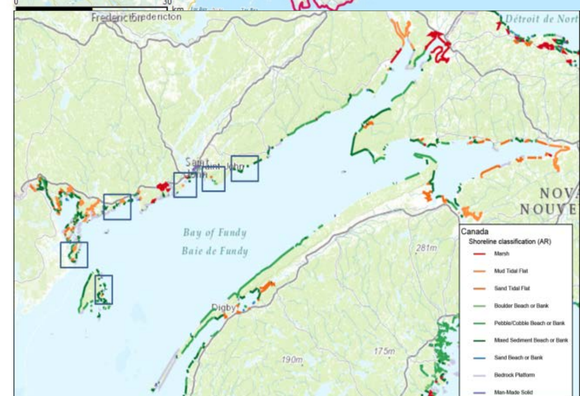
Marine Shoreline Diluted Bitumen Oil Spill Program: Results

- **Results between 2013-2015 for WCTSS phase 1a:**
  - Three field campaigns between 2013-2015 in the Douglas Channel and Haida Gwaii
    - Multidisciplinary team: ECCC, DFO, SCF, WCMRC and consultants
    - Surveyed 25 sites for surface assessment/validation, sampling and baseline physical/chemical analysis, and > 15,000 km by helicopter and segmentation of shorelines
    - Final report on the "Baseline physical geography, biology and chemistry of selected shorelines"
    - Detection and monitoring of oil (including dilbit) on shoreline and in the nearshore water column with the C3 Turner towed fluorometers, GoPro video system and data collection with UAV for shorelines
      - Field trials undertaken with response organisations to review operational requirements
  - Product Experiments: Development of a Science-based Shoreline Treatment Decision-support System
    - Mid-scale studies by Coastal and Ocean Resources on the variables influencing penetration and retention of different dilbit products (AWB + CLB) on shoreline sediment – Report December 2015
  - A review and update of ECCC H&S training and personal protective equipment protocols with the unconventional products was completed including the development of a new diluted bitumen themed H&S training course
  - Delivery of the print-ready 3rd edition of the ECCC SCAT Manual, March 2017

Marine Shoreline Diluted Bitumen Oil Spill R&D Program: Results and to be done

- **Results between 2014-2016 for WCTSS phase 2:**
  - Three field campaigns between 2014-2016 in St. Lawrence: Montreal to Anticosti Island (near Quebec), Port Hawkesbury and the Strait of Canso (Nova Scotia), Saint John and the Bay of Fundy (New Brunswick)
  - Preliminary Detection and Monitoring Studies initiated
    - Monitoring oil movement using satellite oil spill tracking buoys for trajectory modelling
    - Detection of oil on shoreline backshore/nearshore with UAVs
    - Characterization of oil on shorelines using FTIR and in the water column using UV fluorescence techniques
    - Characterization of suspended sediment, natural organic matter and oil in the water column using holographic imaging and laser scattering particle analysis
- **To be done:**
  - Segmentation and classification of 1000s km of shoreline (2 years) and physical/chemical sample analysis for baseline data
  - Continuation of detection and monitoring studies (2 years)
  - Final printed English and French versions, ECCC, 3rd edition of the SCAT Manual (early 2018)





Spill Treating Agents

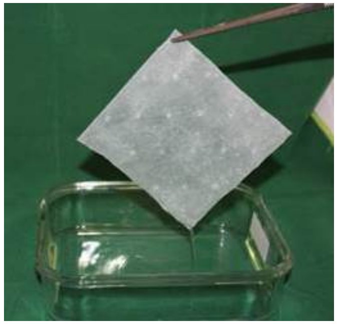
Effectiveness Testing of Chemical Countermeasures on Oil Sands Products

- Dispersants
  - Effectiveness limited by rheological properties: defined threshold values
  - Rapid loss of condensate from dilbits implies a short window-of-opportunity for dispersant use as the rheological threshold is exceeded
  - High asphaltene/resin content of some bitumens may further reduce dispersibility
- Surface washing agents
  - Reduced effectiveness on bituminous residue of dilbits, difficult to penetrate
  - Other oils with mid-range MW components in residue are easier to remove
- Herders
  - Significant reduction in slick size and increase in thickness for all tested oils
  - May be slower to act on viscous oils, up to an hour
- Solidifiers
  - Oil type a minor factor if sufficient mixing provided to facilitate oil-solidifier contact
  - Penetration an issue with viscous oils

Sorbent Performance

Sorbent testing with light, medium, heavy, and viscous oils

- Pads (Type I)
  - Increasing retention with oil viscosity
  - Pad structure provides a surface for bulk adhesion
  - Polypropylene the dominant material, similar performance to others tested
    - Variation with manufacturing process
- Loose sorbent (Type II)
  - Better performance with large-form shapes and lower density
  - Less sorption than pads, penetration limited by discontinuities
  - Socks will effectively sorb viscous oils given sufficient time to penetrate the interior
- Socks (Type III)
  - Limited viscosity effect over the longer term (24 hour)
  - Time required to allow penetration



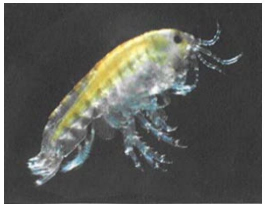
Influence of Temperature on the Limitations of STA Effectiveness

- Dispersants
  - Primary effect of temperature is the change in rheological properties, significant as the limiting threshold is approached
- Surface Washing Agents
  - Low temperatures increase viscosity and reduce penetration
  - Warm water flush necessary as supplement (or alternative)
- Solidifiers
  - General trend to increasing effectiveness with lower temperature
  - Gels below 5 °C, rigid and brittle at -10 °C (non-cohesive)
  - Functionality returns when temperature raised
- Herders
  - Negative buoyancy an issue in fresh water
  - Rheology limiting near freezing

Other Activities

- Development of dioctyl sulfosuccinate (DOSS) analytical techniques
  - Lab method for quantifying concentrations in water, with TPH
  - Exploring degradation characteristics to establish hold times and sample preservative
  - Field sampling guide for DOSS analysis

- Toxicity testing of STAs
  - Objective: to establish toxicity criteria for regulatory listing of permissible products in the offshore

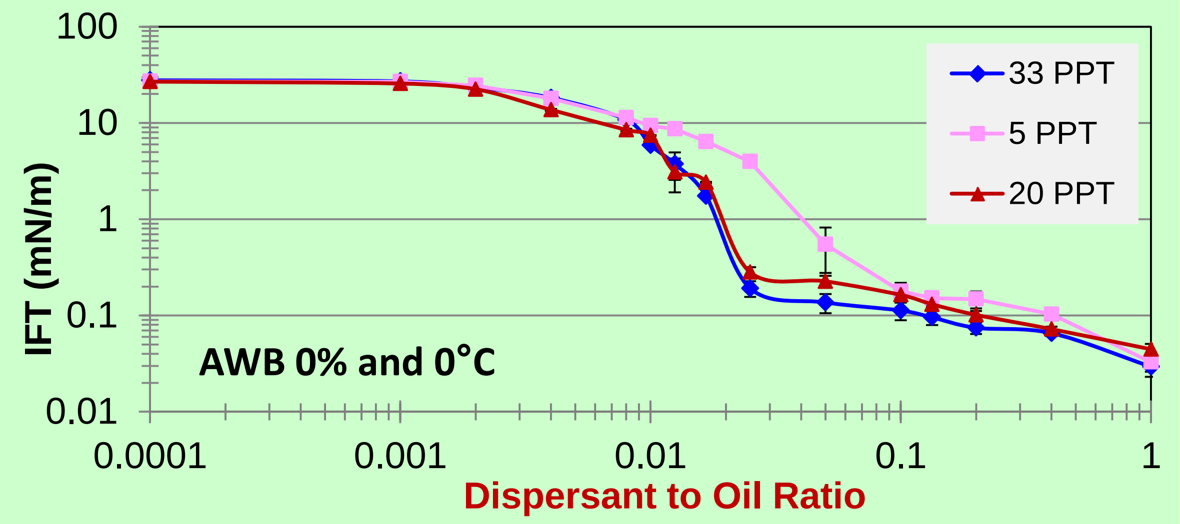


  - Acute lethality, sub-lethal effects, chronic effects
  - Emphasis on dispersants
  - Assess suitability of existing ECCC reference methods
    - Modify to accommodate testing of insoluble mixture (oil)
    - Standardize as necessary

Oil Spill Modelling Research: Goal-1

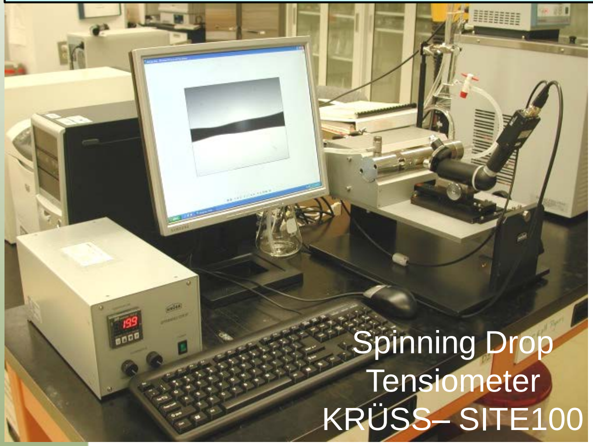
1. Improve modelling of oil dispersion including dispersant effects

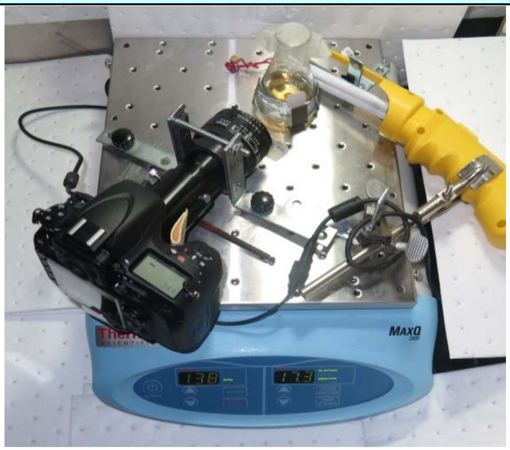
- Develop an extensive and unique database of oil-brine interfacial tension
  - IFT = f(oil, temperature, salinity, DOR)
- Measure variation of oil droplet size under various mixing conditions
  - D = f(oil, temperature, salinity, mixing, DOR)

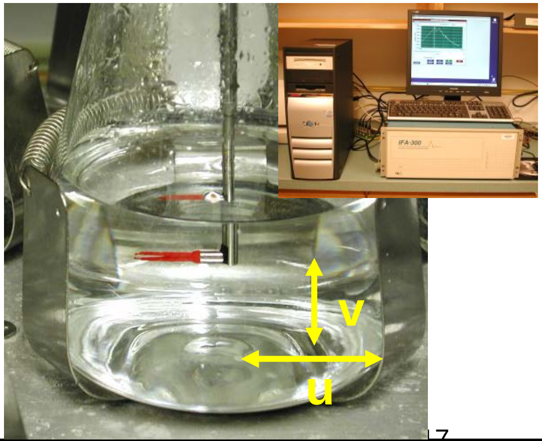


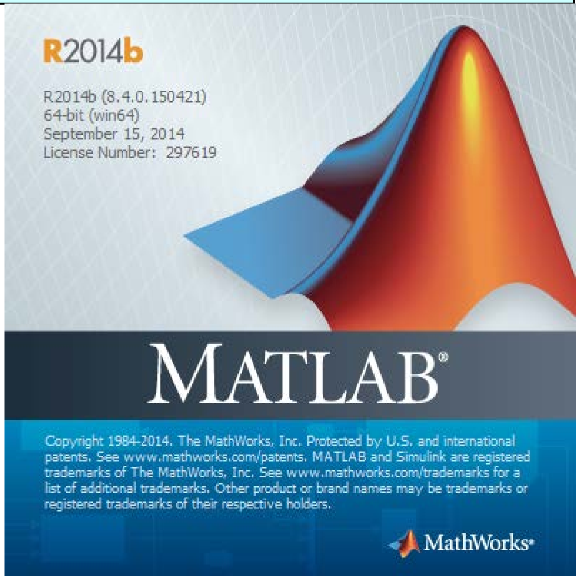
Oil Dispersion: Methodology

Measure IFT	Simulate Dispersion	Image Processing & Spectral Analyses





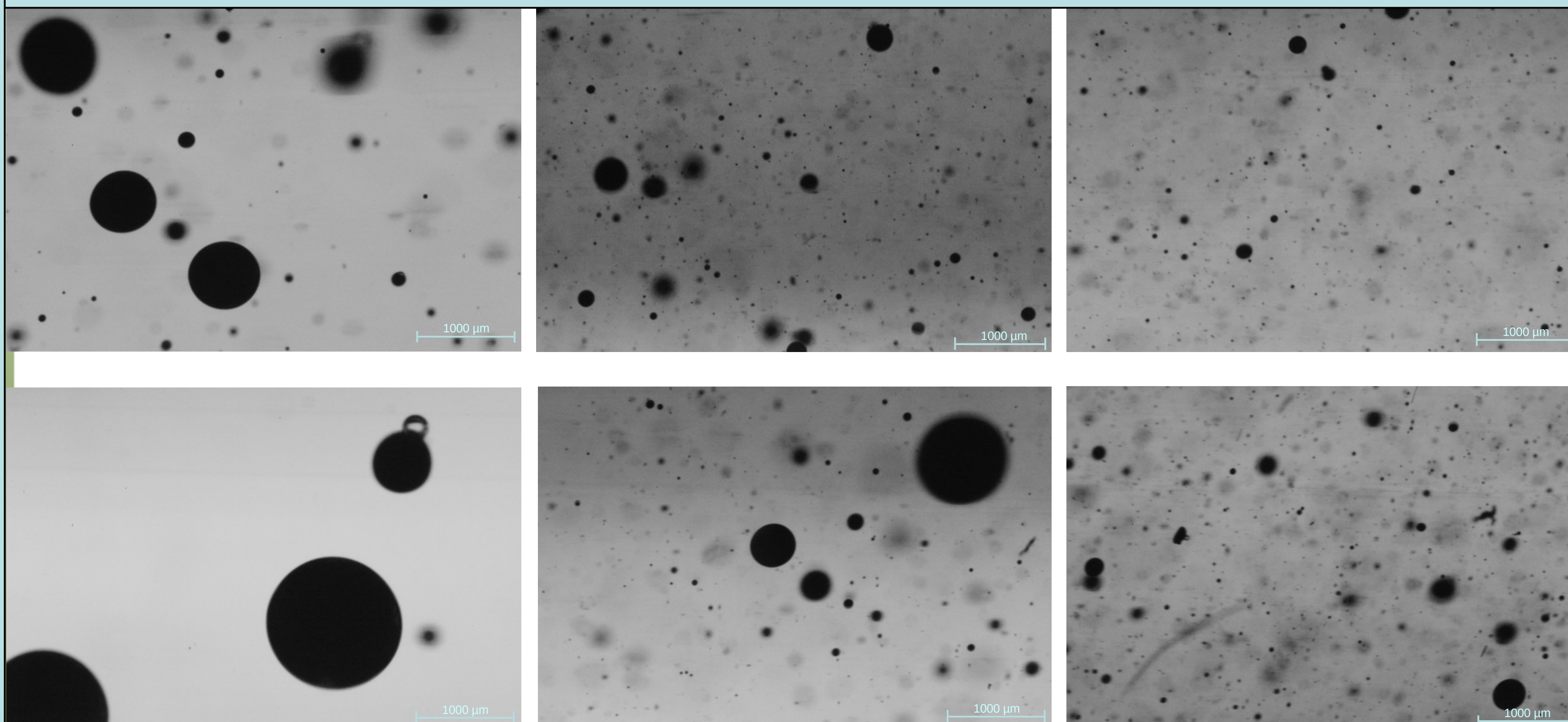




Oil Dispersion: Some Results - D

AWB, 15°C, 33ppt, and 1:40 DOR

	Mixing Frequency = 2.5 Hz	2.7 Hz	2.9 Hz
0 %			
8.5 %			

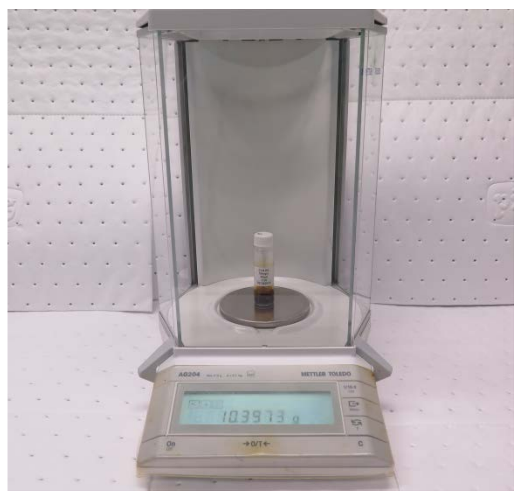


Oil Spill Modelling Research: Goal-2

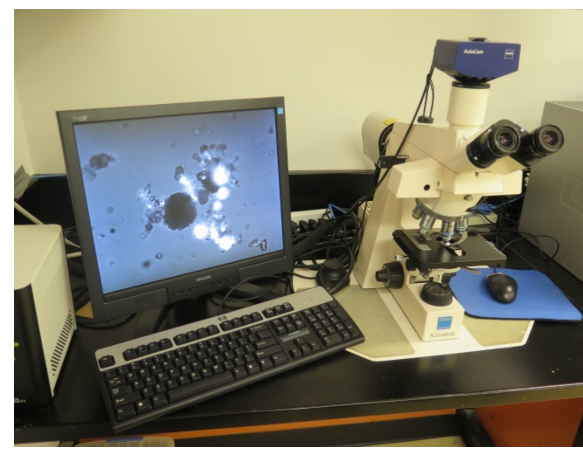
2. Improve modelling of oil sedimentation

- Develop an extensive and unique database on formation of Oil-SPM Aggregates (OSA)
  - OSA= f(oil, sediment, temperature, salinity, mixing, DOR)
- Measure physical properties of OSA
  - D_{OSA}, ρ_{OSA}, V_{OSA}= f(oil, temperature, salinity, mixing, DOR)

Physical Properties



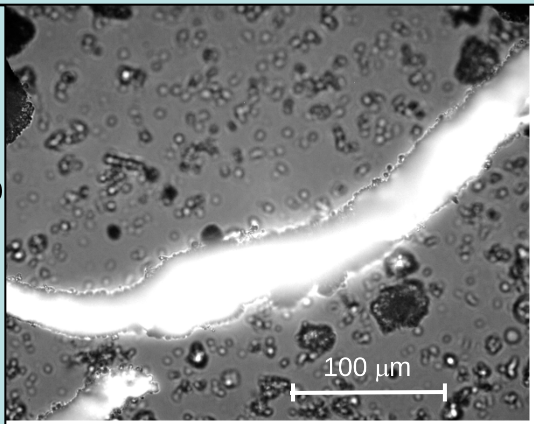
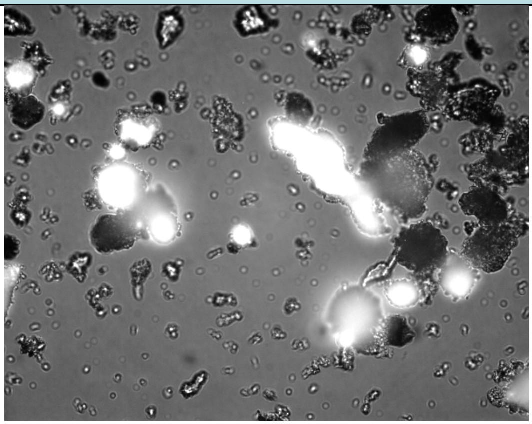
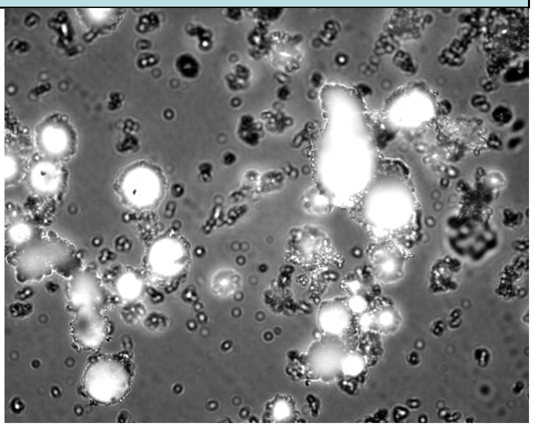
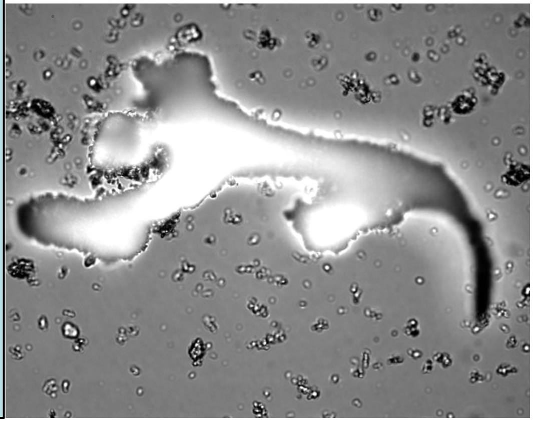
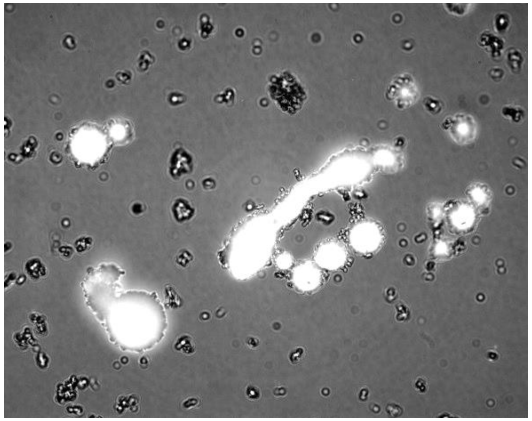
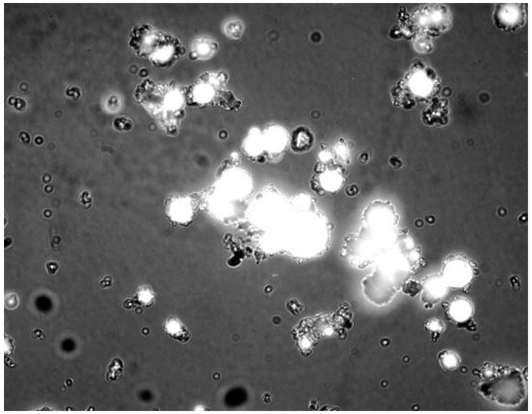
Dilbit Concentration



UV-Fluorescence Microscopy

OSA Formation: Some Results - OSA

Photomicrographs of OSAs using UV-Fluorescence Microscopy
33 ppt water salinity, 100 mg/L of NIST SRM-1941b

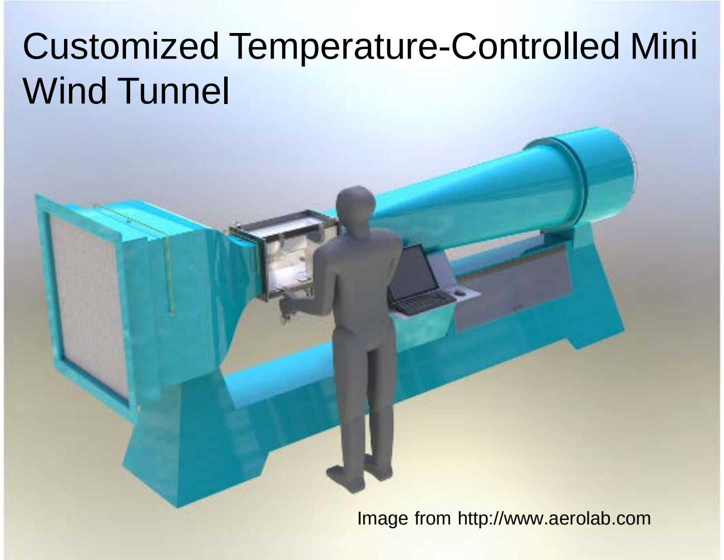
	DOR = 0	1:60	1:20
AWB 0% 15 oC			
CLK 0% 15 oC			

Oil Spill Modelling Research: Goal-3

3. Improve modelling of dilbit evaporation

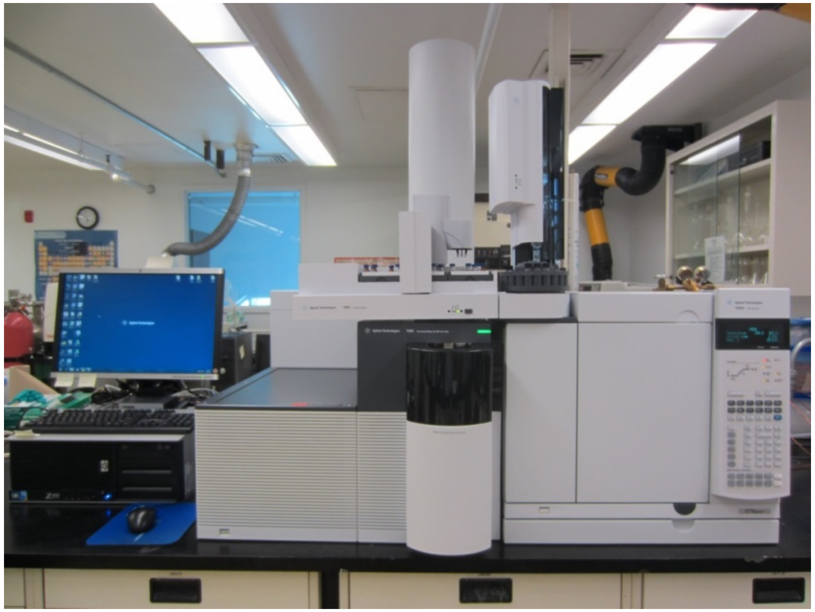
- Develop an extensive and unique database on dilbit evaporation rate

  E_{dilbit}= f(oil, thickness, air temperature, wind speed, DOR)
- Validate & improve existing behaviour models



Application of High Resolution Mass Spectrometry (HRMS) in Oil Analysis

- Gas Chromatography-Quadrupole Time-of-Flight Mass Spectrometer
- Advantages:
  - Improved confidence in quantitation by eliminating those interferences presented with nominal mass chromatograms
  - Rapid screening of target and non-target compounds
- Improved Quantitative Analysis:
  - PAHs
  - S-PAHs and N-PAHs
  - Biomarkers
- Oil Fingerprinting Analysis:
  - Crude oils
  - Petroleum products
  - Environmental samples



GC-QTOF

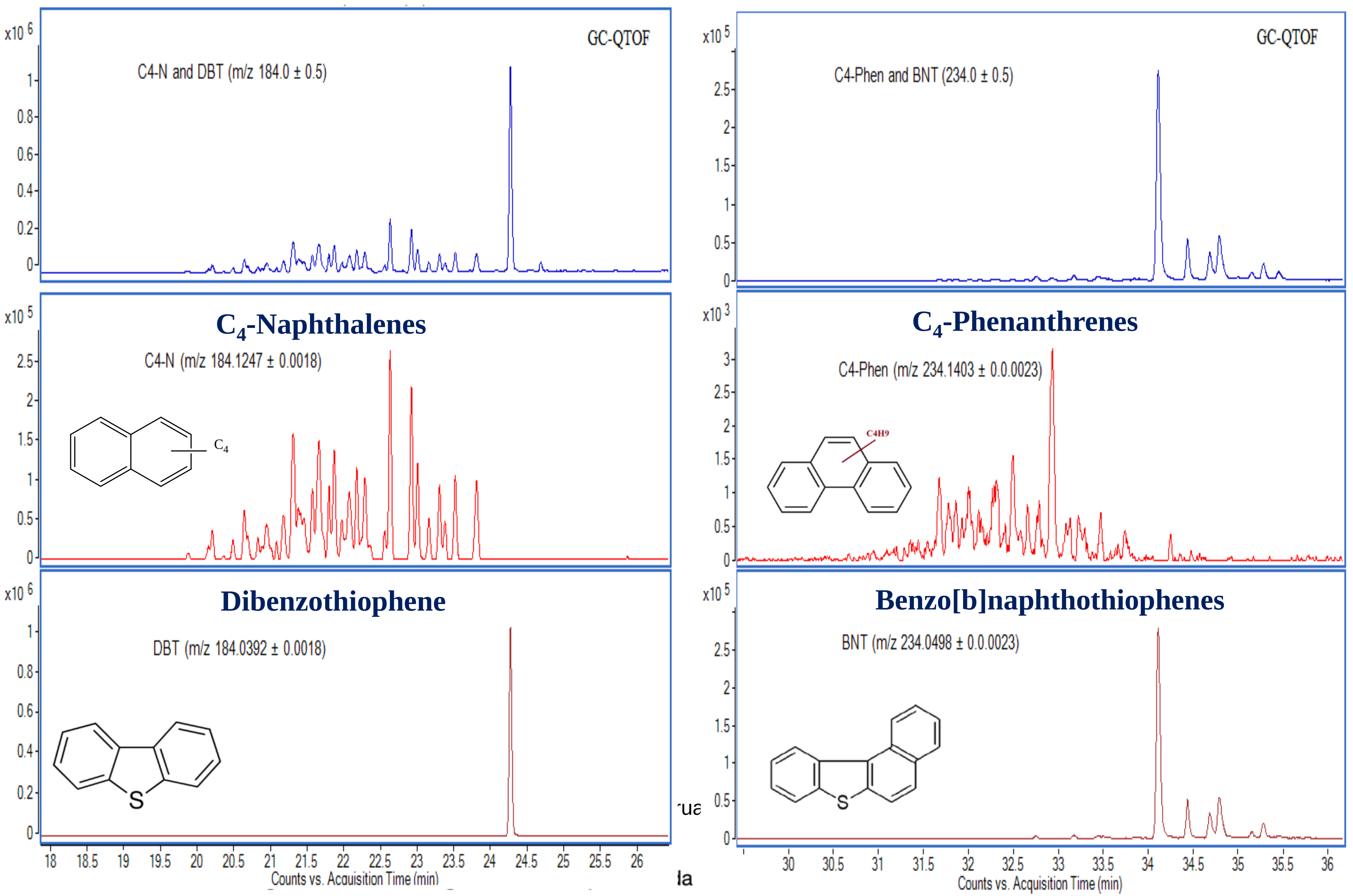
Liquid Chromatography-Orbitrap Mass Spectrometer

- Analytical method developed for the analysis of naphthenic acids (NAs) and naphthenic acid fraction components (NAFCs)

- Various crude oils and petroleum products
- Oil sands bitumen and dilbit
- Oil-contaminated environmental samples
- Oil sands process-affected water (OSPW), investigation of membrane treatment on the chemical composition in OSPW
- Shoreline survey, e.g. Douglas Channel, British Columbia

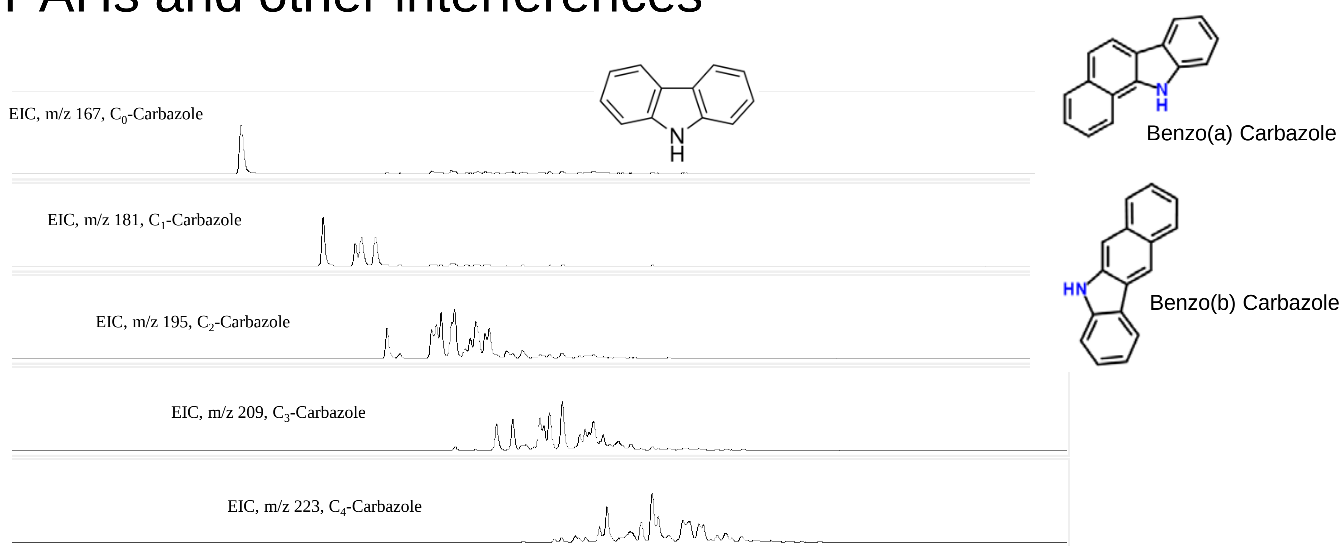


Extracted MS Chromatograms of Target PAHs



Nitrogen Containing Polycyclic Aromatic Hydrocarbons (N-PAHs)

- ✓ Targets N-PAHs: *Indole, Carbazole, Benzo Carbazole and their C1 to C4 alkylated compounds*
- ✓ Fractioning
- • Weak cation exchange (WCX) SPE and silica gel column
- • To separate neutral N-PAHs fraction from saturated hydrocarbons, PAHs basic N-PAHs and other interferences
- ✓ Application
- • Forensic oil spill identification



A typical GC-MS extracted ion current (EIC) chromatogram of C_0 to C_4 carbazoles in IFO180 fuel oil

Development of a Remediation Technology Matrix for Oil Sands-affected Water and Soil

Project funded by NRCan/PERD

Information on technologies that:

- Are mature, commercially available
- Used in the past for remediation of sites contaminated with chemicals which are the same or similar to those in oil sand operations (e.g. petroleum hydrocarbons, fuels, organic solvents, heavy metals, etc.)
- Have the credible and documented performance data

(e.g., assessed under the US Government's Environmental Security Technology Certification Program; Environmental Restoration Program; Superfund Remediation Program, etc.)

- Are applicable for remediation of water and/or soil
- Can be applied *in-situ* or *ex-situ*
- Can treat significant volumes of water and soil

Evaluation of Membrane Filtration for the Removal and Fractionation of Naphthenic Acids

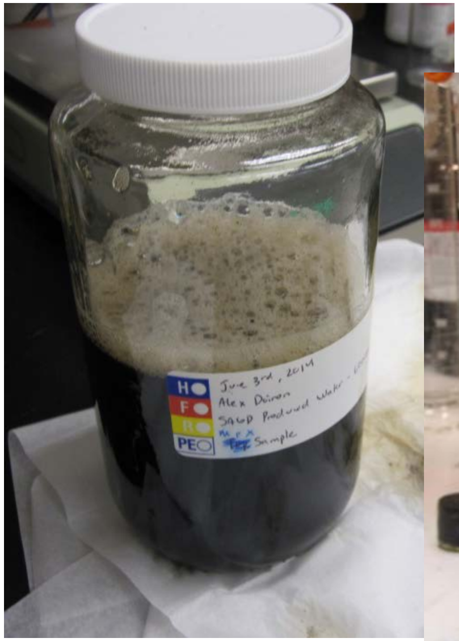
Project funded by NRCan/PERD

- Membrane filtration can be used to
  - Completely remove naphthenic acids from contaminated water, or
  - Separate different groups of naphthenic acids
- Focus on
  - Commercial membranes
  - Separation effectiveness (% removal, membrane throughput)
  - Characterization of different groups of the separated acids (structure, toxicity)
- Initial results look promising

Treatment of Oil Sands Produced Water

(Funded by NRCan/ecoEII. Joint study with Natural Resources Canada and University of Ottawa)

- **SAGD (Steam Assisted Gravity Drainage) produced oily water**
- **Collected on site**
- **Composition**
  - oil sands *bitumen residue*
  - *Salts*
  - *clay*
  - *organic metal ions complex, etc.*
- **Physical properties**
  - *blackish liquid*
  - *suspended fine particles*
  - *strong oil-like odor.*
- **Process train**
  - *1) de-oiling by hydrocyclone*
  - *2) followed by ultrafiltration ceramic membrane (pore size: 3-5 nm)*
  - *3) desalination by reverse osmosis membrane at elevated temperatures*



Feed Water

Treated Water (Permeate after de-oiling)

Treatment of Oil Sands Produced Water: Test results

- Total solvent-extractable materials: ***~ 95% rejection***
- Total undissolved emulsion material: ***~ 100% rejection***
- Total petroleum hydrocarbons (non-polar organics)
  - Total saturated hydrocarbons: ***~ 100% rejection***
  - Total aromatic hydrocarbons): ***~ 100% rejection***
- Naphthenic acids fraction components (Polar organic): ***~ 80% rejection***
- ***High rejection (greater than 99%)*** for major hardness components (Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+}) from 20 to 70^{o}C on three tested RO membranes
- Hardness: reduced to ppm level for major cations

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Thank you!