C-NLOPB Spill Prevention and Response Forum, January 12-14, 2021

NRPOP - Northern Region Persistent Organic Pollution Control Laboratory

- *An Overview of Oil Spill Research*

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NRPOP LAB
Northern Region Persistent Organic Pollution Control Laboratory

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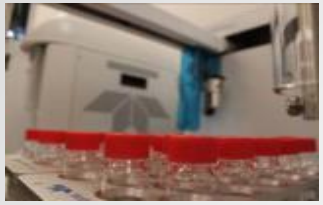
Major Sponsors





Northern Region Persistent Organic Pollution Control (NRPOP) Lab

First of its kind in Canada with national and international recognitions

Major funding **from CFI, NSERC, NL Government, PRNL**, etc.

Target Pollutants

- **Persistent** and **organic** pollutants – petroleum hydrocarbons and by products (esp. **oil spills**), polycyclic aromatic hydrocarbons (PAHs), produced water, marine (ballast/bilge) wastewater, other industrial oily wastewater, contaminated sites, etc.
- **Emerging** pollutants (EPs) in ocean and coastal environments - chemical surfactants, pesticides, flame retardants, disinfection byproducts, pharmaceutical and cosmetic products (PPCPs), nano-particles, microplastics, etc.

Target Environments

- Cold regions including North Atlantic, Arctic and sub-arctic areas
- **Marine and coastal environments**, etc.

Research Team

Professors

- **3** core professors, **10+** adjunct/associated professors, and 30+ collaborators globally

Postdocs and Students

About **20-30 trainees at any time** incl. 4+ postdocs/RAs, 10+ PhD, 10+ masters students, and some work-term UG students; hosted 40+ visiting scholars worldwide; grudated students well placed in adademia, industry and government

International Collaborations

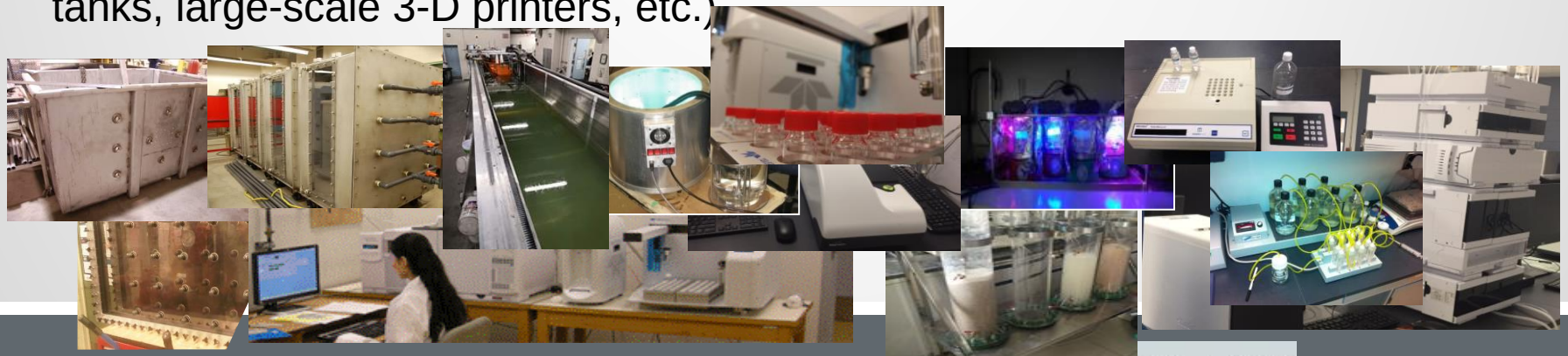
- **Institutional** collaborations with Univ of British Columbia, McGill Univ, Univ of Victoria, McMaster Univ, Dalhousie Univ, Univ of Regina, Univ of California Berkeley, Stanford Univ, Cornel Univ, Maryland Univ, Univ College of London, Nanyang Technological Univ, Peking Univ, Beijing Normal Univ, Ocean Univ of China, etc.
- **Governmental** collaborations with Environment Canada, Fisheries and Oceans Canada, Natural Resources Canada, NL Department of Environmental Conservation, US EPA, US NOAA, CSIRO, UNDP, etc.
- **Industrial** collaborations with PRNL, ExxonMobil, Suncor, Equinor (Statoil), ECRC, ABS, SINTEF, Cedre, Vale Inco, Nestle, etc.

➔ *multiple-scale R&D and real-world applications*

Major Research Expertise ➔ marine/inland oil spill response and cleanup, contaminant fate, transport and effects, marine/coastal pollution prevention & mitigation, advanced water/wastewater treatment, environmental nanotech, environmental biotech, site remediation, process simulation & control, system optimization, risk/impact assessment, AI-aided decision making, etc.

Featured Facilities

- **Advanced analytical instruments** (GC/GC-MS, GC-FID/ECD, HPLC-MS/MS, IC, AAS, TPH, TOC, spectrometers, AES, viscometer, contact angle goniometer, etc.)
- **Biological and nanomaterial devices** (PCR, fermentor, Microtox, respirometer, bio-safety carbinet, glovebox, freeze-dryer, NanoSight, LISST, microreactors, etc.)
- **Physical simulation chambers/models** (e.g., batch-/bench-/pilot-scale reactors/tanks incl. cohosting a 3.6m soil tank and 12m wave/spill tank)
- **Data/image processing tools and modeling software -** GNORM, OSCAR, MEDSLIK, LINGO/LINDO, ArcGIS, AutoCAD, Matlab, Worldviz VR, Hololens, etc.
- **Faculty of Engineering** - towing/wave tank, deep-water tank, ice tank (w wind tunnel), cold rooms (-20°C; x3), AUV and gliders, etc. (NRC – 200m ice/wave tanks, large-scale 3-D printers, etc.)



Oil Spill Research

+ NRPOP LAB
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Area 1: Biosurfactant producers and production

Area 2: Bio-aided oil pollution mitigation

Area 3: Enhanced monitoring and analysis

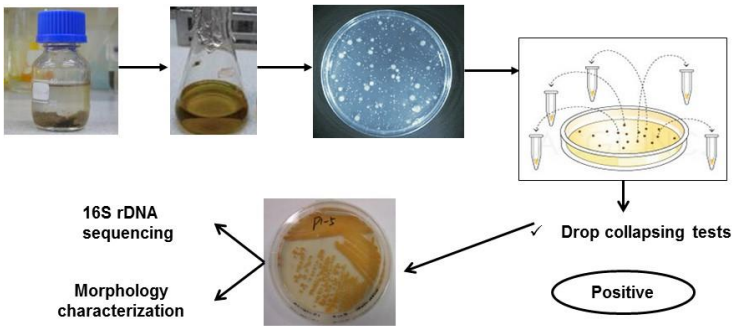
Area 4: Oily wastewater treatment

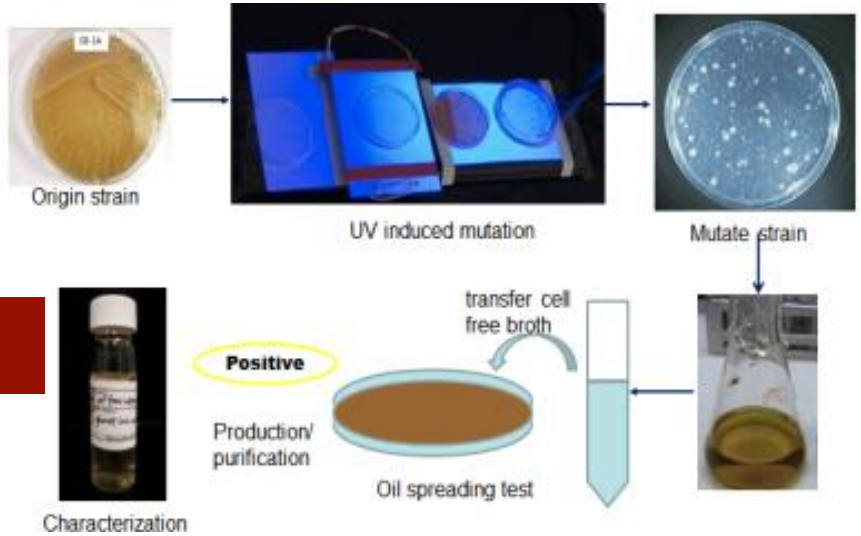
Area 5: Dynamic simulation, integrated assessment and intelligent decision making

~100 refereed journal publications and 6 patents/disclosures in the past 5 years
(e.g., JHM, EP, WR, BT, FEE, JCP, STOTEN, Chemospere, JEM, MBP, EnvSoft, ESPR, JEI, RSC Adv, GA)

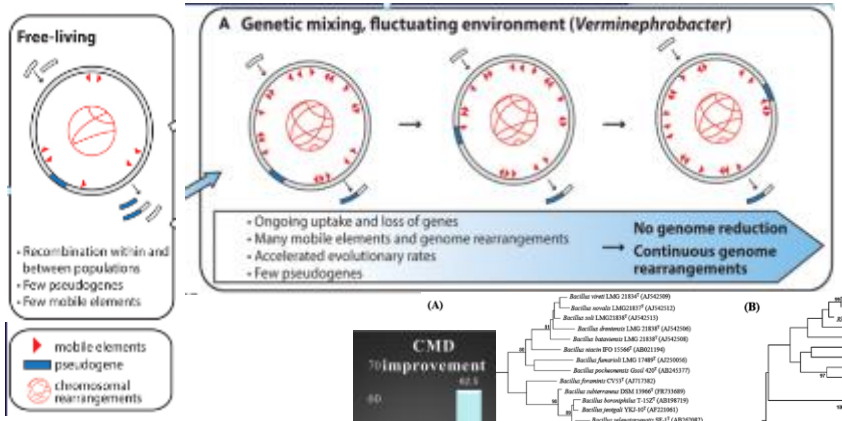
Research Area 1: Biosurfactant Producers and Production

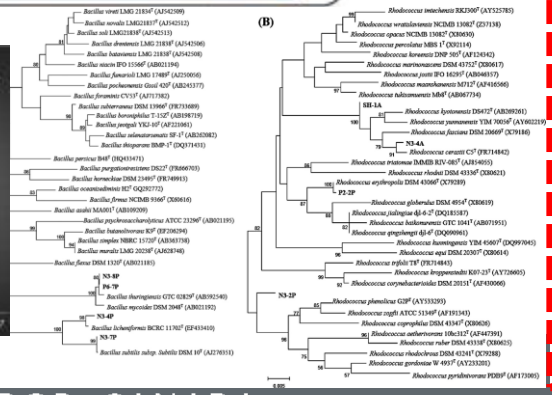
1-1: Biosurfactant producer screening and genetic engineering





"improved bacterial mutation technology" has a great significance in the future





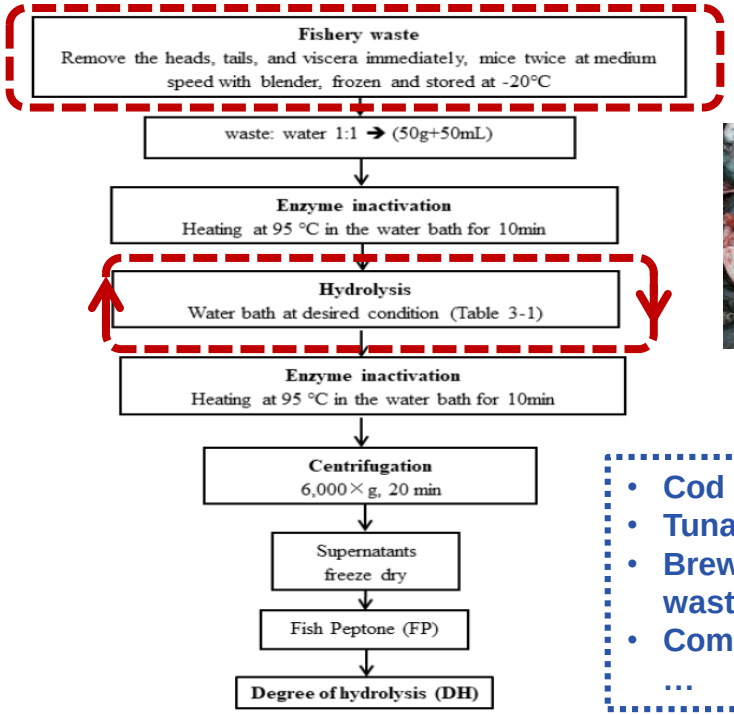
Research outputs:

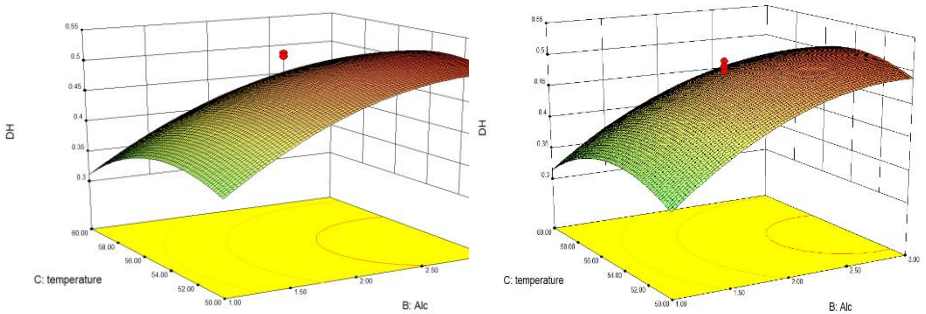
1. **140+ surfactant production strains** were screened from the North Atlantic ocean and coasts, including one new strain and **one first discovered strain** with surfactant production ability as well as a variety of characteristic strains

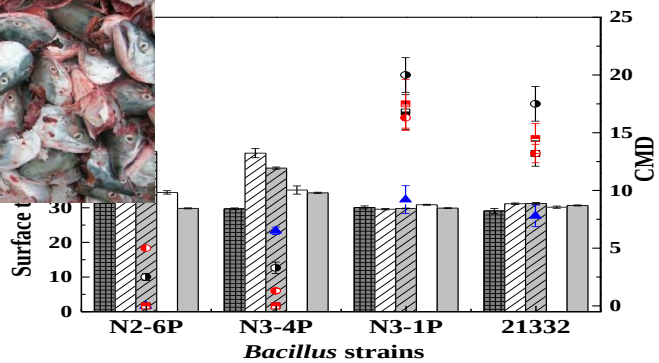
2. By genetic shuffling, ultraviolet mutation and enzyme technology, etc. high efficient mutation strains were obtained. The best strain can increase production capability with over **200+ times CMC**.

1-2: Waste based biosurfactant production

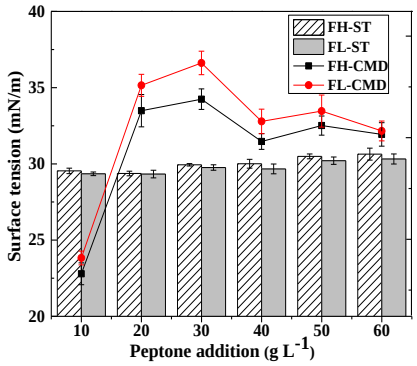
Large scale biosurfactant production face challenges from high production cost ➔ selection of economical raw material is important

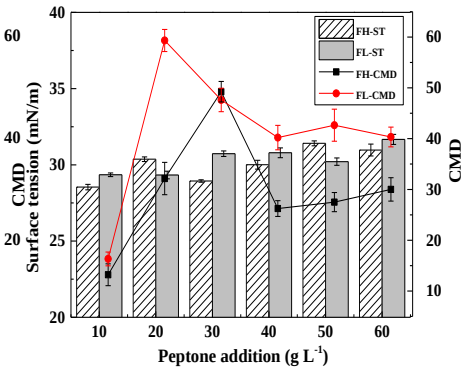






- Cod waste
- Tuna waste
- Brewery waste
- Composting
- …



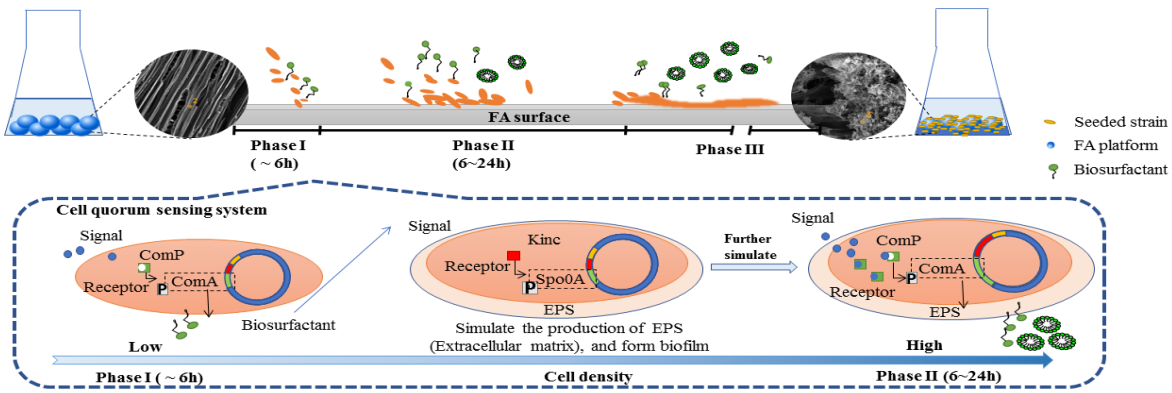


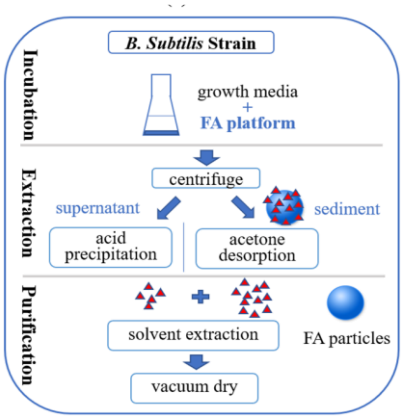
Research outputs:

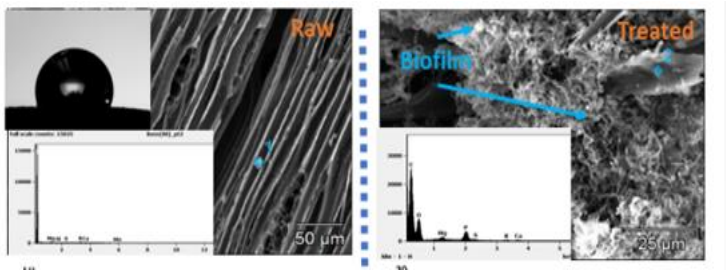
1. Various local waste resources (e.g., cod, tuna, brewery, etc..) were evaluated and proved as a promising biosurfactant producing substrate.
2. A cost reduction (10%-20%) was achieved with a productivity enhancement (~10%)

1-3: Cultivation system design and advancement

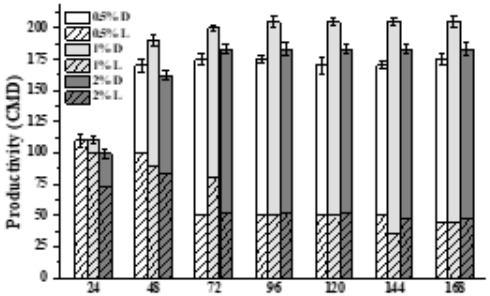
The development of fermentation system is expected to ➔ ease production process, enhance productivity with stable product quality

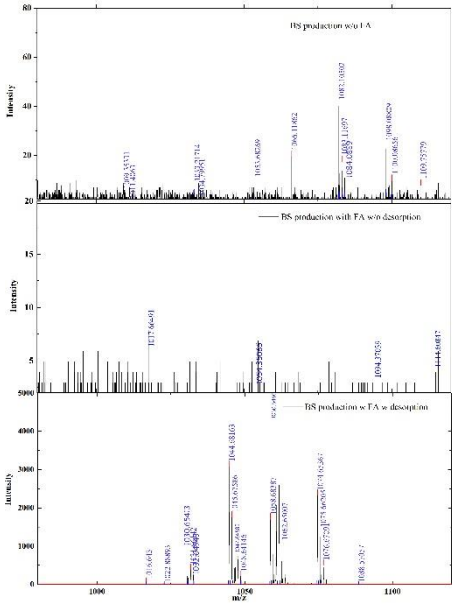






Time (h)	0.5% FA Zeta Potential (ξ)	0.5% FA SD (%)	1% FA Zeta Potential (ξ)	1% FA SD (%)	2% FA Zeta Potential (ξ)	2% FA SD (%)
0	-3.45	6	-9.54	6	-10.89	2
6	-13.78	5	-15.05	5	-13.43	5
12	-14.48	4	-15.05	3	-14.08	3
18	-17.17	3	-15.08	6	-14.48	6
24	-19.13	1	-16.52	1	-14.77	5





Research outputs:

1. Investigated the immobilization of biocatalyst on porous carrier nano-material ➔ to enhance cell density ➔ promote biosurfactant productivity
2. Improved the understanding of cultivation setups ➔ shed light on the application of fixed bed biofilm reactor for catalyzing bioproduct generation

Research Area 2: Bio-Aided Oil Spill Cleanup

2-1: Bio-dispersion for marine oil spill response and cleanup

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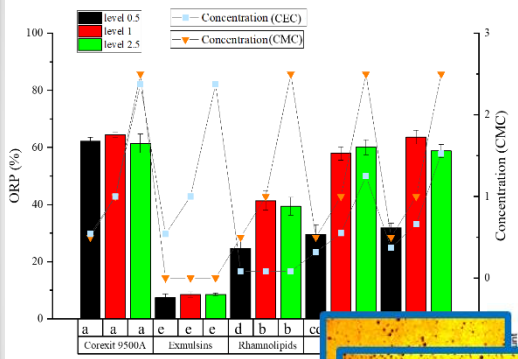
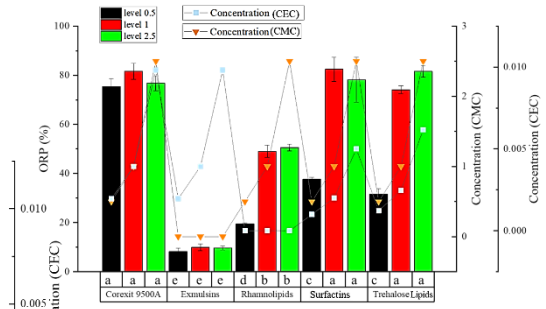
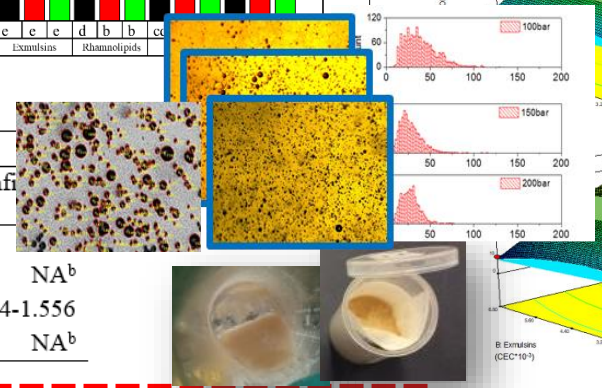
Performance of biosurfactant based dispersants? ➔ surface-active properties, effectiveness, toxicity

Surface-active parameters	Units	Surfactins	Rhamno-lipids	Trehalose lipids	Exmulsins	Corexit 9500A
CMC	(mg/L)	13.01	1355.71	199.16	500512.65	32.41
Minimum surface tension	(dynes/cm)	28.98	39.97	34.90	57.06	39.96
CEC	(g/L)	1.56	>1016	19.37	14.73	1.98
Maximum E24	(%)	60.00	0.00	63.33	65.00	56.25
CMC/1000CEC	1	0.0083	<0.0013	0.010	33.98	0.016



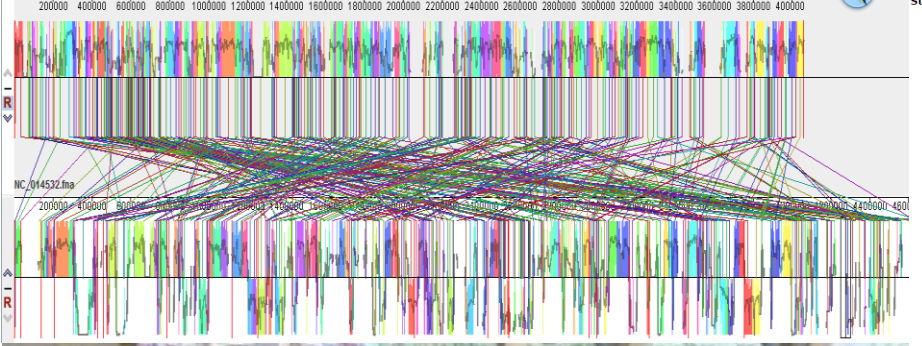


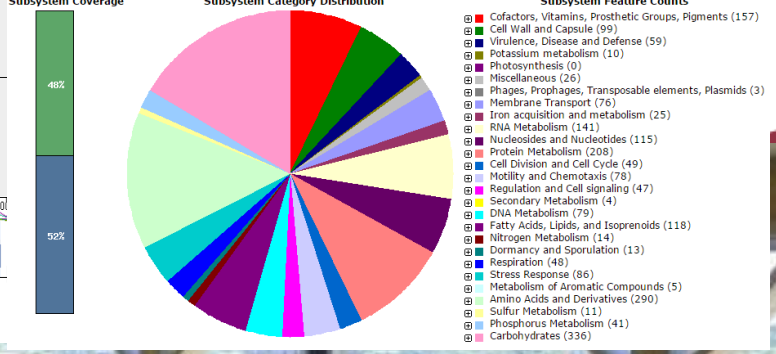


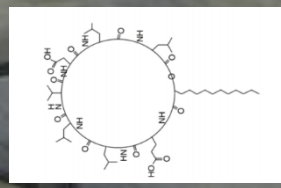
Biosurfactants	EC50 (g/L)			
	5 min exposure	95% confidence range	15 min exposure	95% confi
Surfactins	0.243	0.122-0.486	0.255	
Trehalose	>6.150	NA[b]	>6.150	NA[b]
Rhamnolipid	0.968	0.730-1.285	0.977	0.614-1.556
Exmulsins	>5.005	NA[b]	>5.005	NA[b]

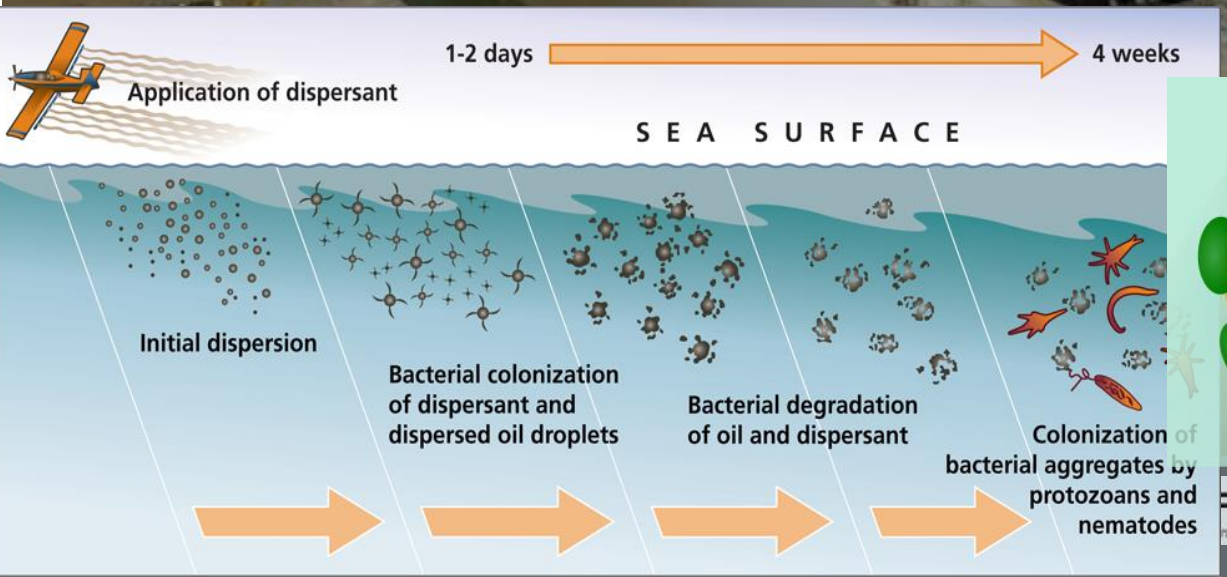
Research outputs:

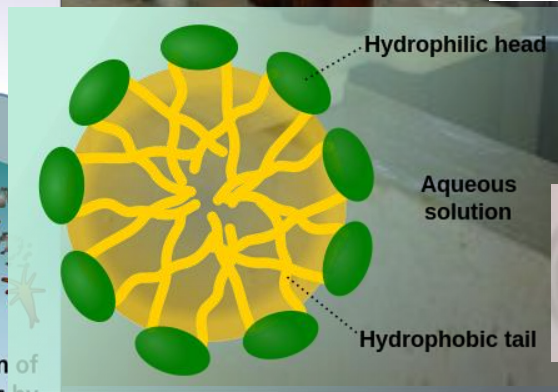
1. Biosurfactants generated by different bacteria ➔ evaluated as candidate for dispersant development (Surfactin/Trehalose lipids)
2. The optimum oil dispersion effectiveness achieved ➔ when combining the abilities of surface/interfacial tension reduction and emulsion stabilization in a balanced manner
3. Oil spill and dispersion in deep water (up to 3,000 psi or ~2000 m deep) by chemical and biological dispersants

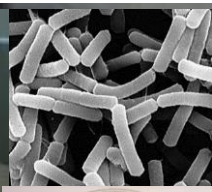












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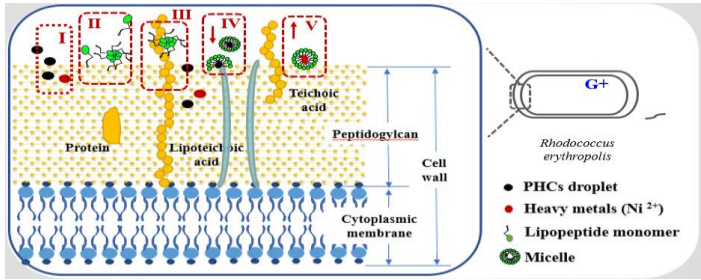
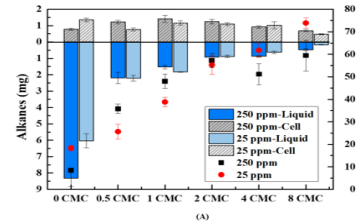
2-2: Bio-enhanced coastal washing and bioremediation

- Mechanism evaluation of biosurfactant enhanced bioremediation





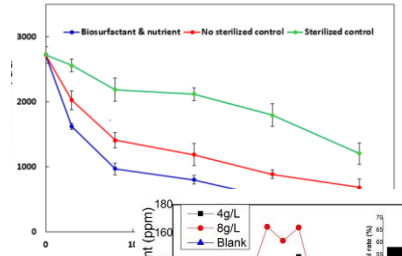
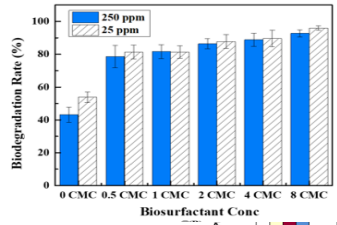


Figure 4.2 Kinetics of the P
nutrient. Data are presented



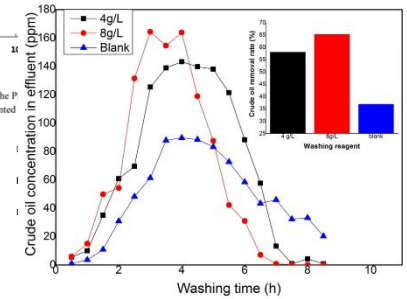
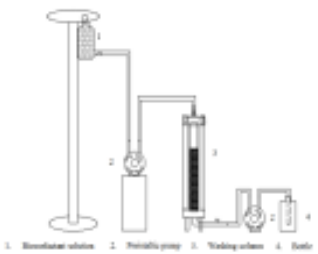
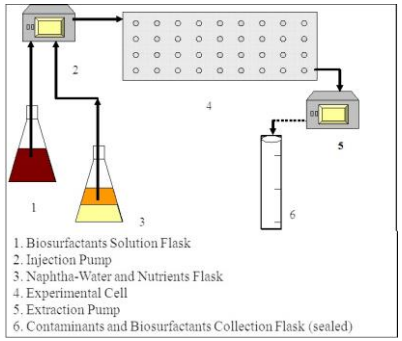


Fig 6 Effect of biosurfactant concentration on enhanced crude oil removal in soil washing system

- Biosurfactant enhanced flushing/bioremediation





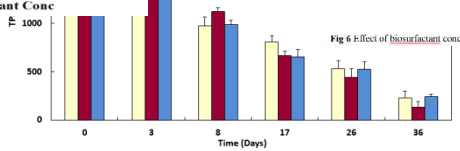
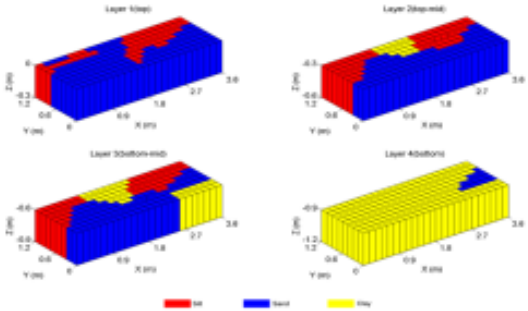


Figure 4.3 The biodegradation behavior of PHC by the supplementation of increased amounts of rhamnolipids and nutrients to investigate the degradation potential of the microorganisms.

- Pilot scale evaluation of biosurfactant enhanced soil remediation

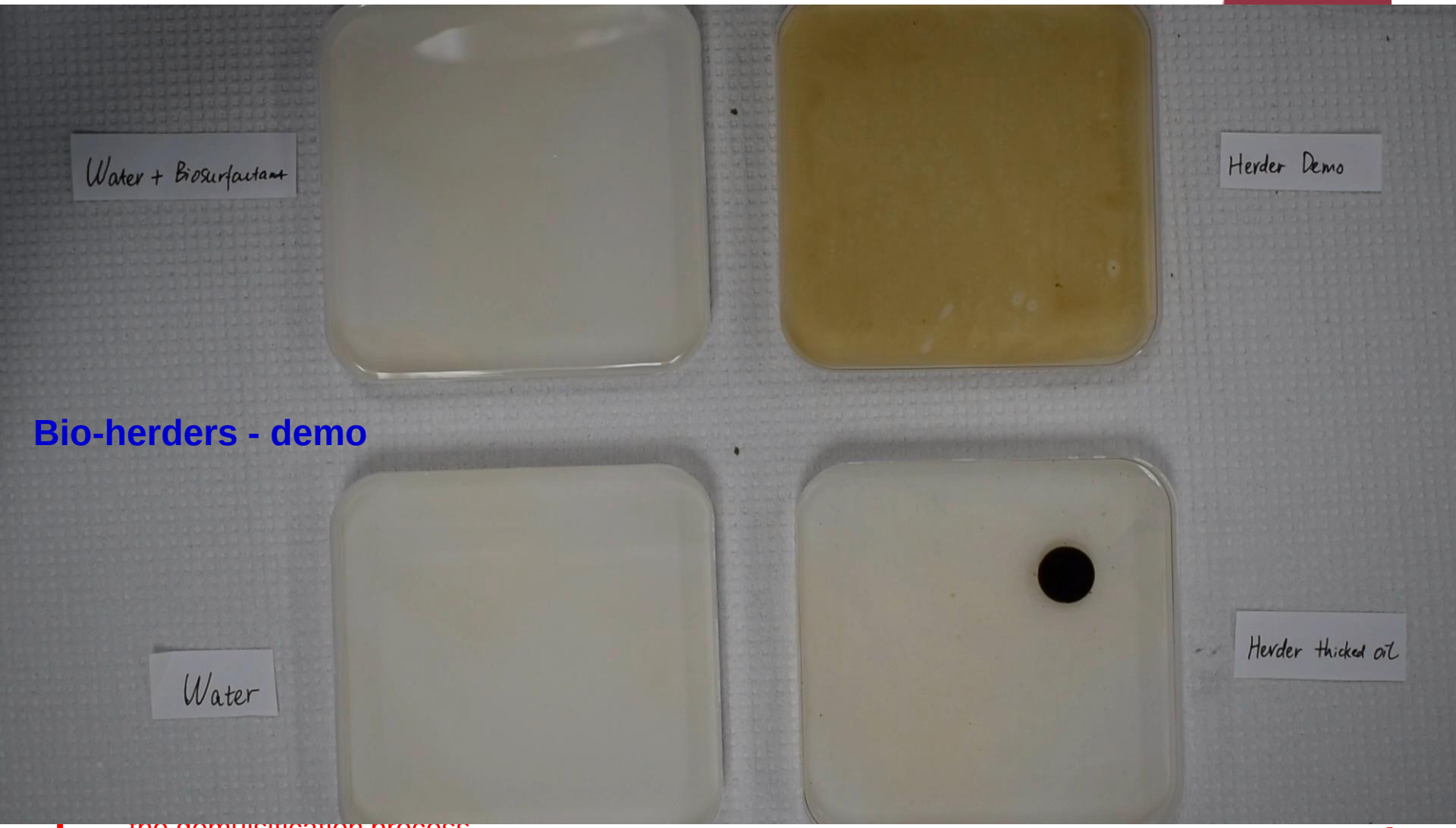


Research outputs:

1. Bio-enhanced coastal remediation technologies ➔ evaluated in multi-scales for oil pollution cleanup and heavy metal removal

2. Physical and numerical simulation, system optimization, and their coupling → cost reduction and efficency improvement

2-3: Bio-demulsification and bio-herding for oil spill response



Bio-herders - demo

the demulsification process

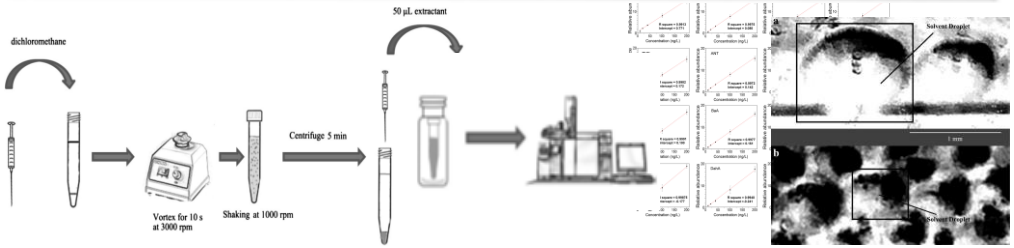
2. Contribute to the development of biological demulsification of oily wastewater stream

Research Area 3: Environmental Monitoring and Analysis

3-1: Advancement of oil analysis

• VSA/LLME-GC/MS analysis

Current methods	Complex	Time/solvent consuming	Hard to trace in environment
vs			
New methods	Rapid and simple	Low-expense and toxic	Efficient for intensive detection



• Compound-specific stable isotope analysis (CSIA)

Monitoring and quantification tool ➔ identify the biodegradation pathway of dispersed oil ➔ CSIA

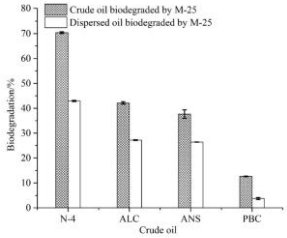


Fig. 3. The biodegradation of TPH of four crude oil and dispersed crude oil.

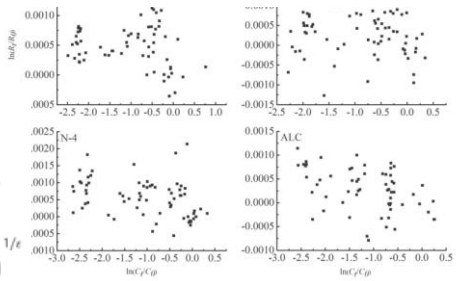
Table 1. Stable isotope enrichment factors of n-alkanes during biodegradation of dispersed crude oil (DCO)

DCO	Regression equation	R^2	ε (‰)	B (%)
ALC	$\ln(R_t/R_0) = -2.5\times10^{-4}\ln(C_t/C_0) - 1.5\times10^{-5}$	0.67	−0.25	99.9
ANS	$\ln(R_t/R_0) = -7.0\times10^{-5}\ln(C_t/C_0) + 4.7\times10^{-4}$	0.81	-7.0×10^{-2}	99.6
PBC	$\ln(R_t/R_0) = -3.7\times10^{-5}\ln(C_t/C_0) + 2.2\times10^{-4}$	0.83	-3.7×10^{-2}	99.9
N-4	$\ln(R_t/R_0) = -2.2\times10^{-4}\ln(C_t/C_0) + 3.3\times10^{-4}$	0.76	−0.22	99.5

$$\delta^{13}C_{sample} = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000$$

$$\ln\frac{R_t}{R_0} = \ln\left(\frac{\delta^{13}C_t + 1}{\delta^{13}C_0 + 1}\right) = (\alpha - 1)\ln\frac{C_t}{C_0} = \varepsilon \ln f$$

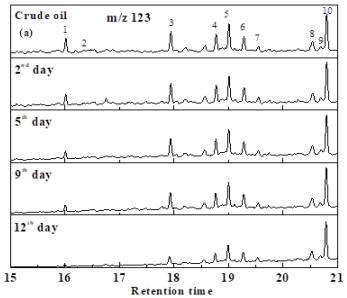
$$B = 1 - f = 1 - \left(\frac{\delta^{13}C_t + 1}{\delta^{13}C_0 + 1}\right)^{1/(\alpha-1)} = 1 - \left(\frac{\delta^{13}C_t + 1}{\delta^{13}C_0 + 1}\right)^{1/\varepsilon}$$

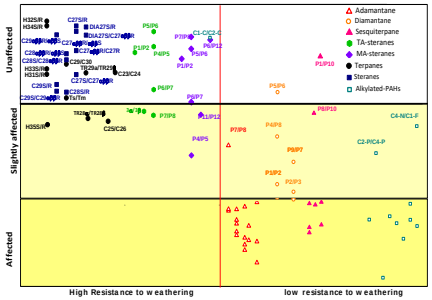


thmic plot (Rayleigh equation, Eqn (2)) correlating isotopic composition with residual concentration of individual n-alkanes for n isotope fractionation during biodegradation of dispersed crude oil.

• Oil biomarkers and fingerprinting

Dispersed oil ➔ Physiochemical weathering / Microbial degradation ➔ Biomarkers distribution





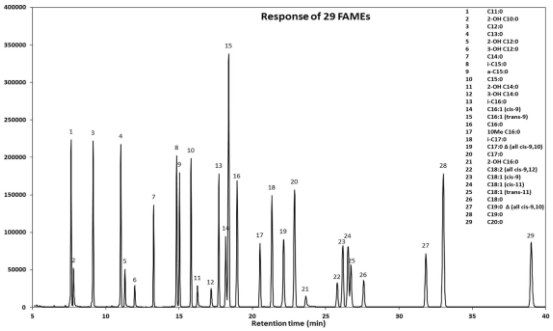
Research outputs:

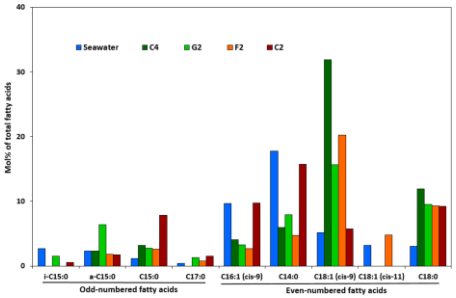
- **Oil compound analysis in complex matrix:** Vortex- and Shaker-Assisted Liquid–Liquid Microextraction (VSA-LLME) coupled with (GC-MS) ➔ trace levels (> 10 ng/L) of dissolved PAHs in offshore produced water
- **Biomarkers and fingerprinting:** screening of reliable biomarkers ➔ identification of spill source and weathering status of dispersed oil
- **CSIA** ➔ quantitation method to monitor the biodegradation of naturally/chemically dispersed oil in ocean environment

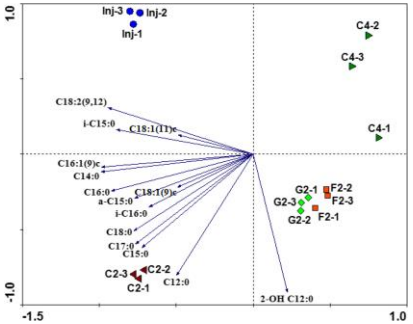
3-2: Phospholipid fatty acid (PLFA) based microbial community analysis

- **Sulfate-reducing bacteria (SRB) qualification/quantification in reservoir samples**

Extraction of Lipids
↓
FAMEs production
↓
GC-MS analysis
↓
Statistical Correlation
↓
PLFAs Characterization
↓
Optimization

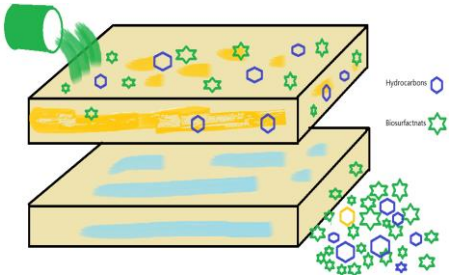


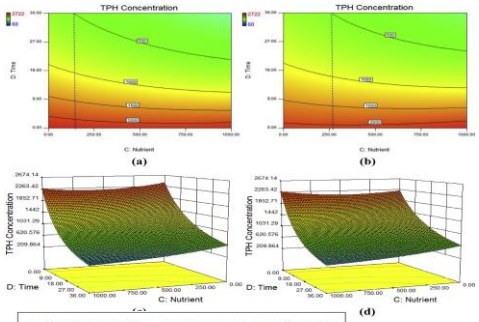


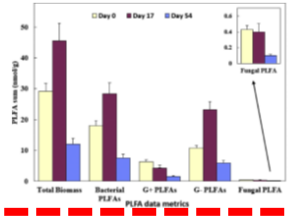


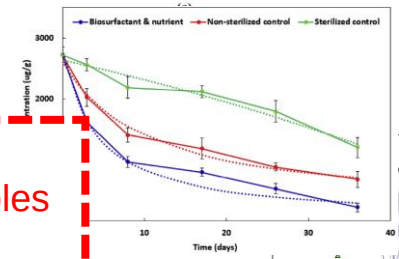
- **Microbial community analysis during oil biodegradation**

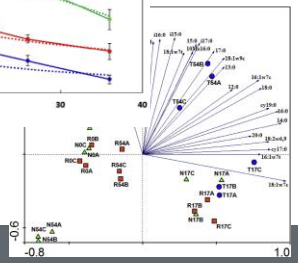
Bioremediation
↓
FAMEs production
↓
GC-MS analysis
↓
Statistical Correlation
↓
PLFAs Characterization
↓
Optimization











Research outputs:

1. **Development of PLFA quantification method** ➔ routine analysis of samples with high oily and salinity properties in marine environment ➔ elucidate dynamic changes of the microbial community structure, and associated biodegradation mechanism during biodegradation
2. Application: PLFA analysis for profiling microbial communities in offshore produced water, oil contaminated soil and sludge samples

Research Area 4: Oily wastewater treatment

4-1: Enhanced oxidation processes and nano-microbial enhancement for wastewater treatment and reuse

Enhanced oxidation processes (EOPs): ozonation + UV/LED + nano-catalysts/MOFs + ultrasonication + biosurfactants + continuous flow micro-reaction + microbial fuel cells

Management technologies: process simulation + process control + system optimization

Barrels of produced water samples

Batch scale UV treatment vessels | Bench scale treatment reactors

UV-enhanced Photo Oxidation Approaches ↔ Hybrid Oxidation System ($UV/O_3/TiO_2$)

Key testing parameters: UV (wavelengths, strength, exposure time), pH, temperature, photo catalyst (type & dose), ozone (concentration, flow rate, time), biosurfactant (dose &type) etc.

Process control & Experimental optimization

Produced water sample pretreatment

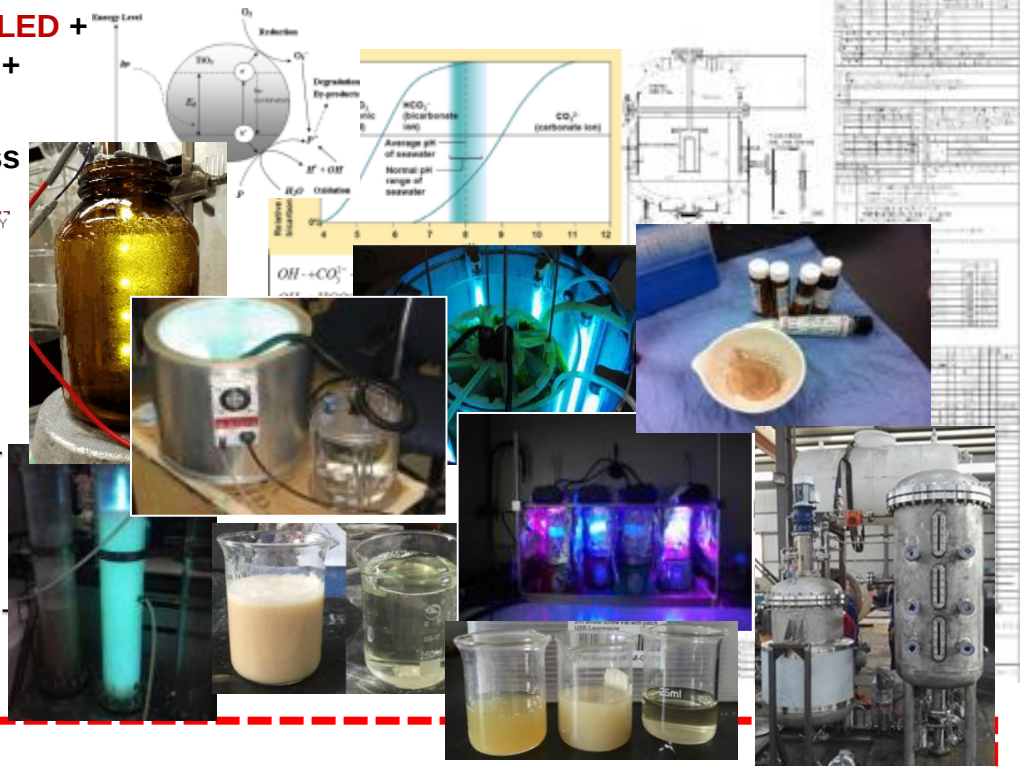
Solid Phased Extraction (SPE) ↔ Liquid Phased Micro-Extraction (LPME)

Instrumental (GC/MS) Analysis & Data processing

Photo degradation dynamics evaluation ↔ Toxicity and risk evaluation

System integration and application

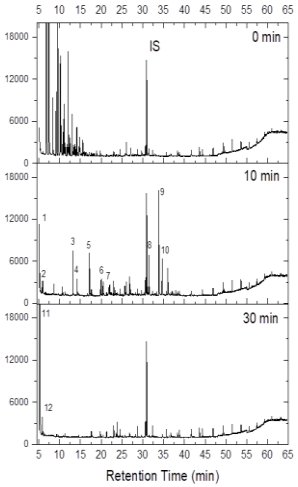
Lab/sea-trial tests



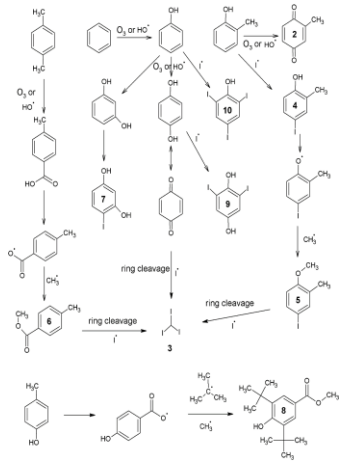
Research outputs:

1. Nanoscale catalytic materials ➔ High activity, good stability, makes reaction possible under visible light
2. Integration with microbial enhanced methods ➔ reduce cost and make process green and less environmental impact
3. Design of EOPs reactor and the optimization of reaction conditions➔ make the technology possible for industrialization, and finally realize recycling, and "zero pollution emissions"
4. Multi-scale tests and application of the coupling use of the EOPs and nano-microbial enhancement for industrial wastewater treatment and reuse (oil & gas, petrochemical, pesticide, pharmaceutical, shipping, etc.) with high cost-efficiency

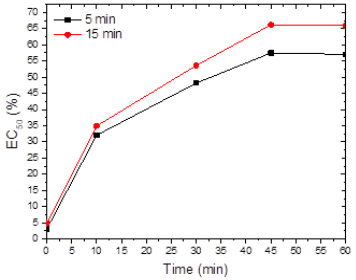
Oil removal

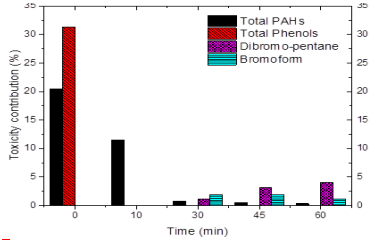


Intermediates/pathways

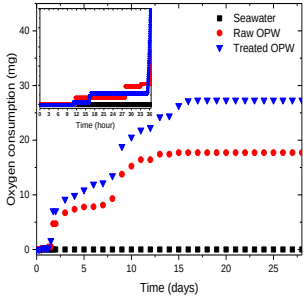


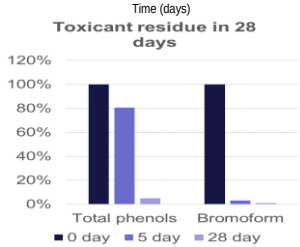
↓ Toxicity

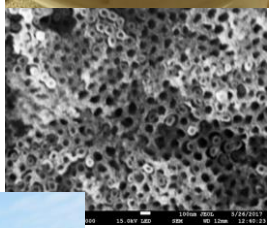




↑ Biodegradability



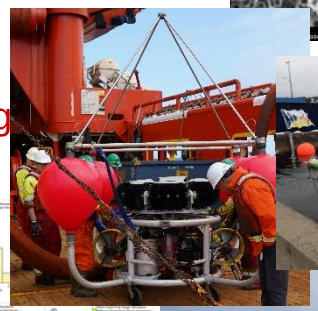


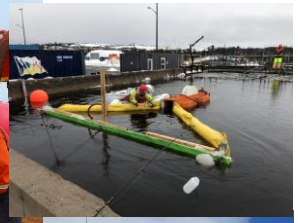


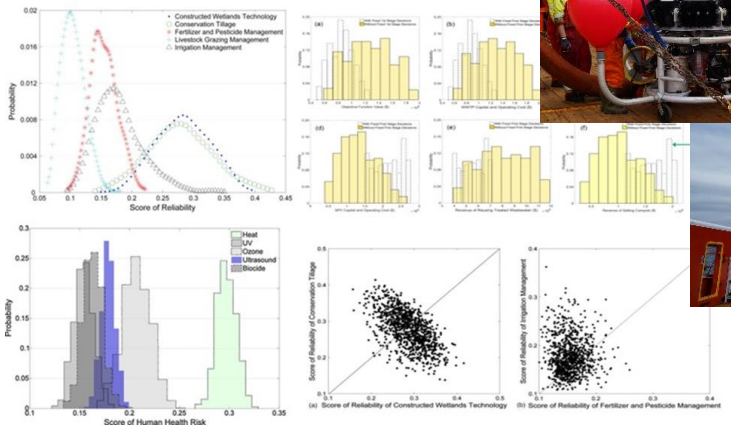
Key research outputs:

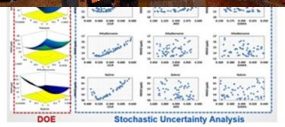
- Nanoscale catalytic materials ➔ High activity, good stability, makes reaction possible under visible light
- Mechanisms/pathways ➔ unveils HCs removal, degradation pathways and intermediates, toxicity change during the process
- Integration with enhancement methods ➔ reduces cost and makes process green and less environmental impact
- Design of EOP reactors and optimization of reaction conditions➔ industrialization and "zero pollution emissions"
- Provide feasible and effective expressions of uncertainties and simulation/assessment results into environmental decision-making

Simulation-based process control and operation planning

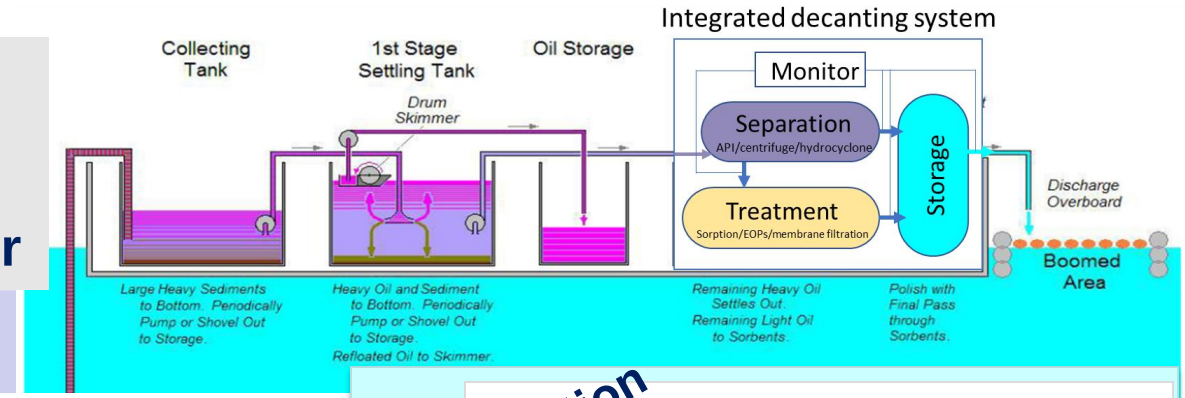


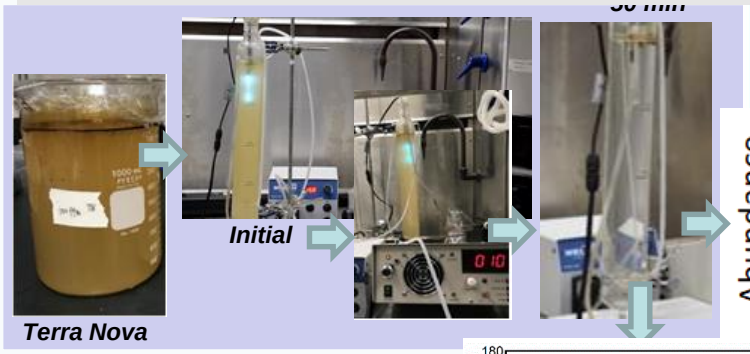


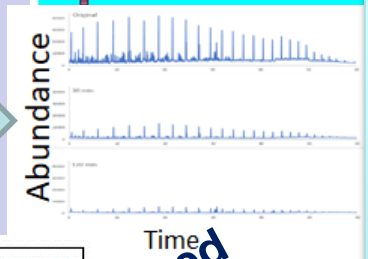




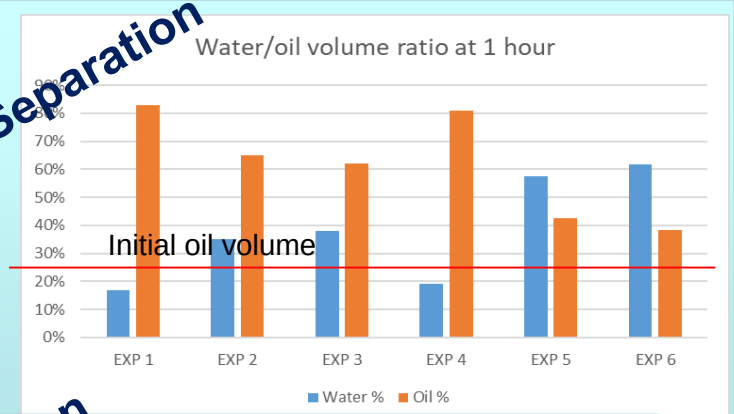
4-2: Integrated decanting system for marine oil spill response and on-site treatment of decanted water

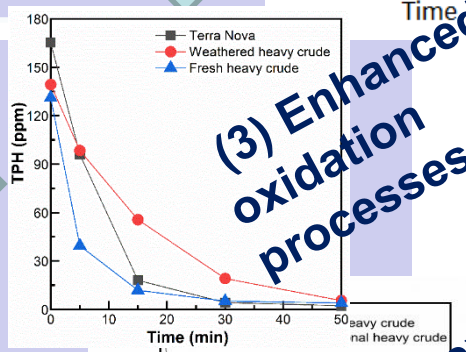






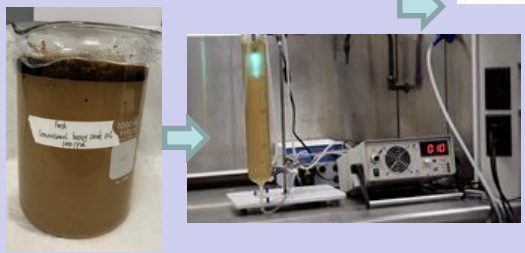
(1) Separation

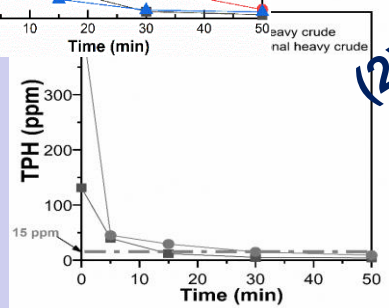




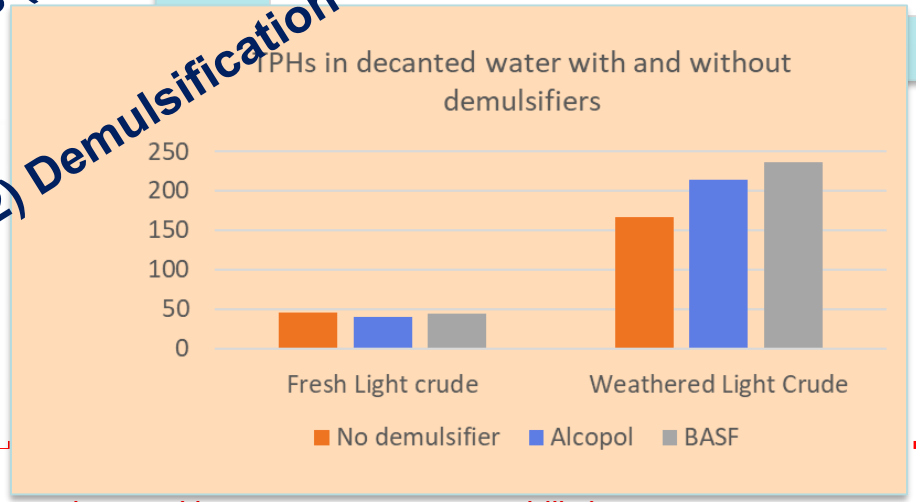
(3) Enhanced oxidation processes (EOP)

Fresh/Weathered heavy crude





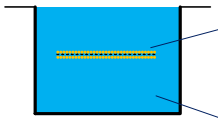
(2) Demulsification



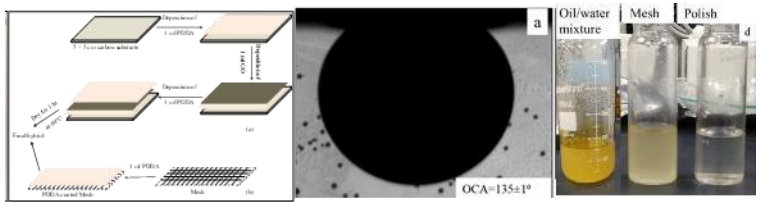
High-efficiency and potential for applications in fields:

- Oil spill response ➔ on-site decanting for disposal at sea (save time and improve response capability)
- Light crude, fresh oil, weathered oil ➔ demulsifiers can increase oil solubility and decrease decanting time (up to 50%)
- Enhanced oxidation processes (EOP) ➔ TPH (~400 ppm) reduced to <15 ppm (IMO std.) within 15-30 min; Removal rate (50 min): TPH: 98% & PAH (NAP): 93% ➔ promising for discharge at sea
- **Integration of gravity separation + demulsification + EOP ➔ from O/W of 30/70 to >99% separation and TPH <15 ppm!**

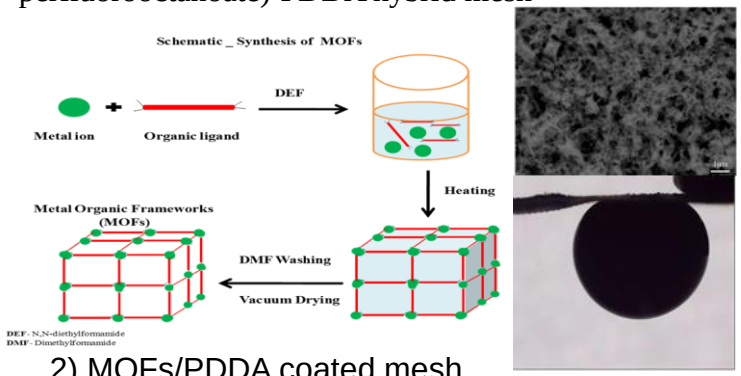
4-3: Hydrophilic Mesh and Activated Carbon for Oil Water Separation (Decanting)



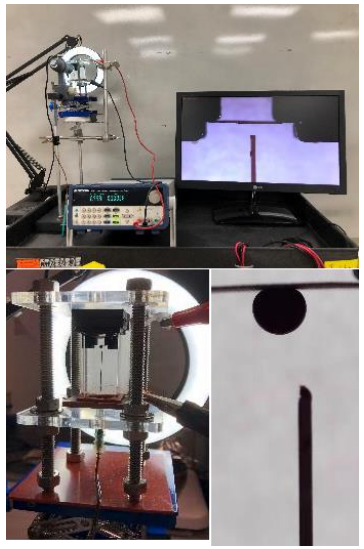
Dip Coating



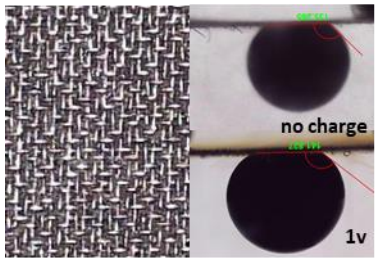
1) Poly(diallyldimethylammonium-perfluorooctanoate) PDDA hybrid mesh



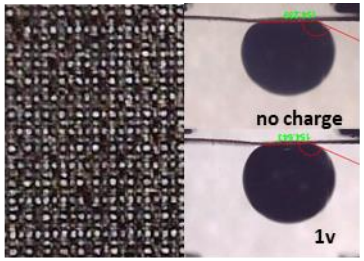
2) MOFs/PDDA coated mesh



Electrical Charge



3.1) Wood based fly ash coated mesh



3.2) Oil fly ash coated mesh

Research outputs:

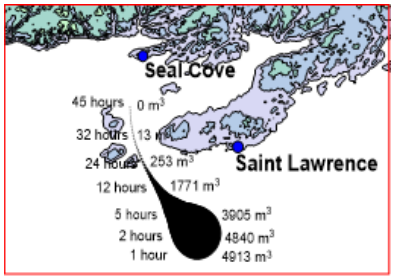
High potential for on-site treatment of decanted water.

1. Reach up to 99% TPH removal if combining with a polishing process using graphene oxide.
2. The mesh showed 98% TPH removal with water polishing. After treating by the mesh and polishing, the TPH in water was 30 ppm and 5 ppm respectively (initial 290 ppm).
3. Applying a low voltage of charge improves the surface hydrophilicity of the mesh in seawater. An oil water separation setup using this technique will be developed to test the TPH removal efficiency.

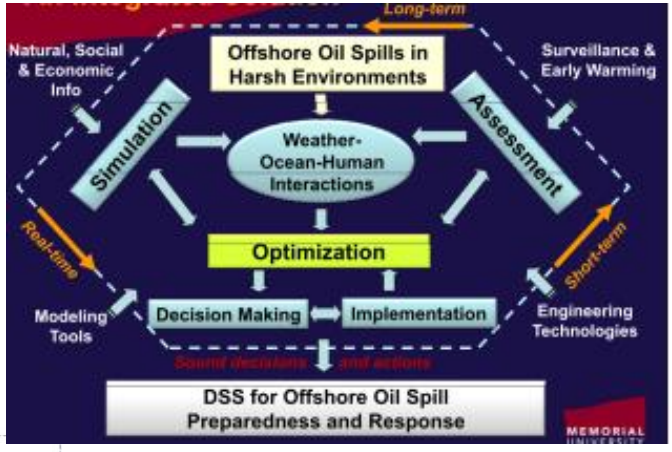
Research Area 5: Dynamic simulation, integrated assessment and intelligent decision making

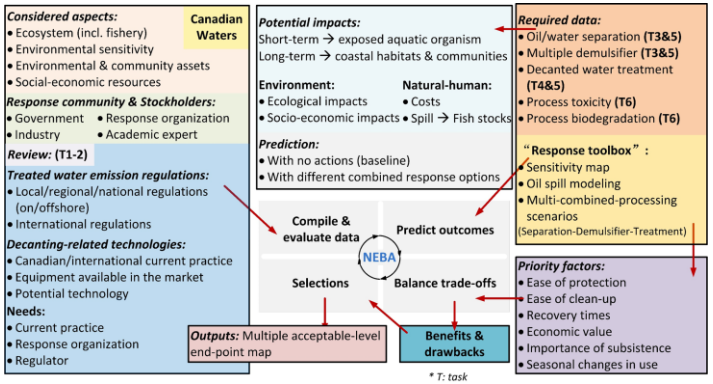
5-1: Integrated decision support systems for environmental emergency management

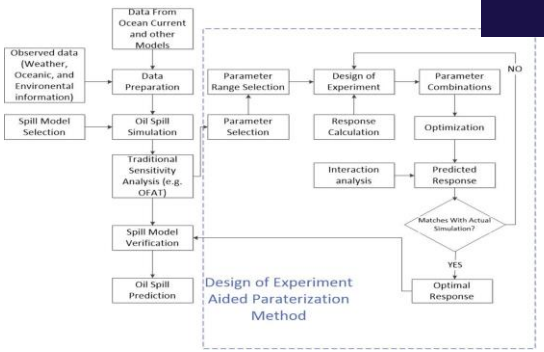
Environmental emergency (e.g., oil and chemical spills) ➔ strong needs in effective response decision making tools

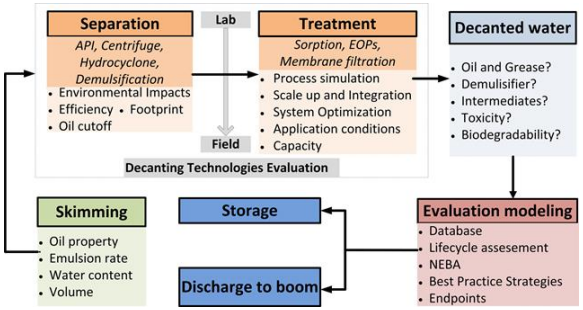


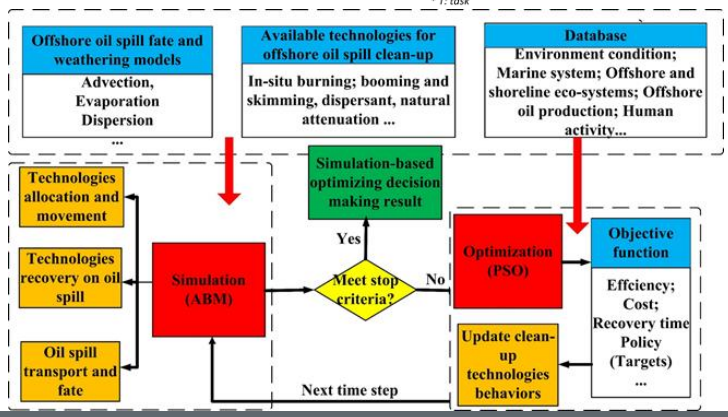
Spill risk assessment and response modeling



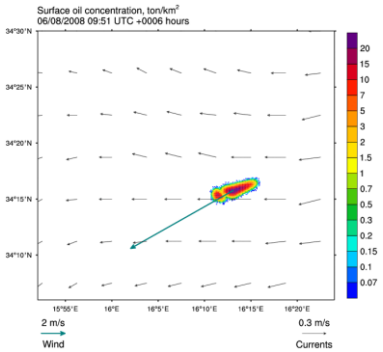


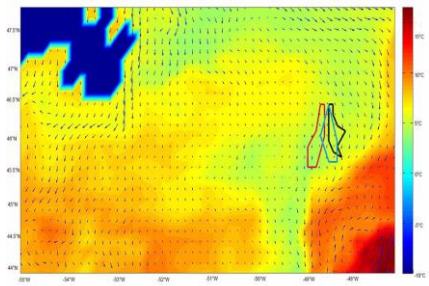


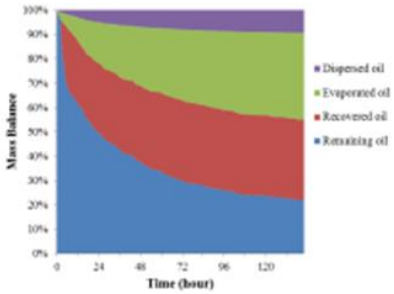


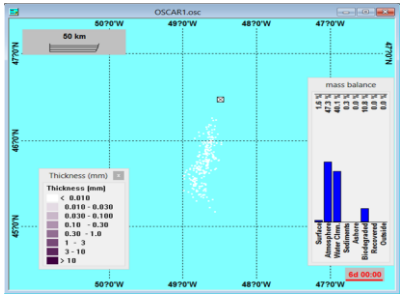


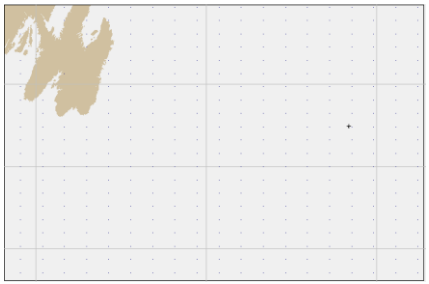
Oil spill simulation: GNOME and OSCAR + uncertainty analysis

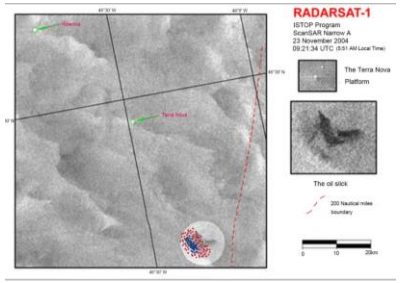




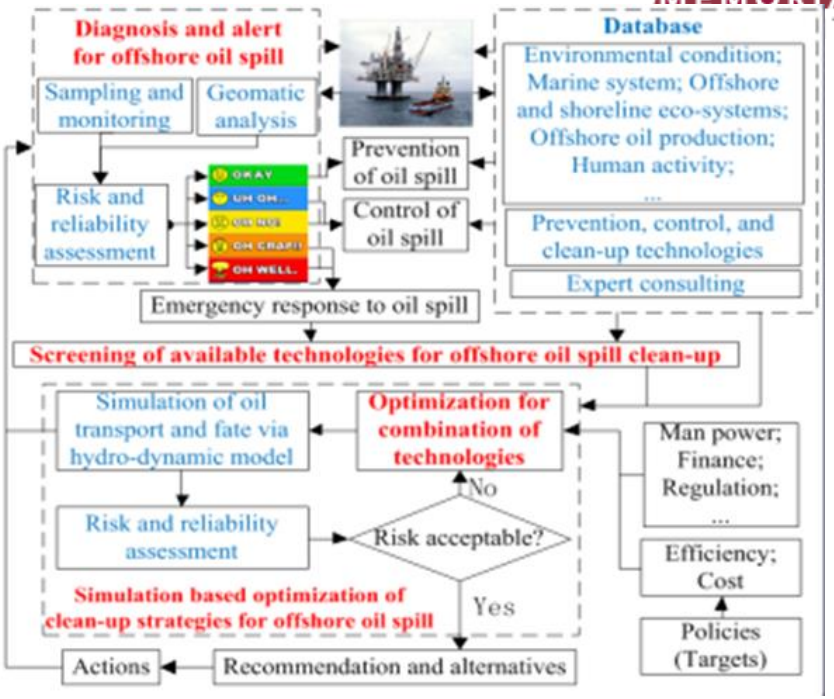


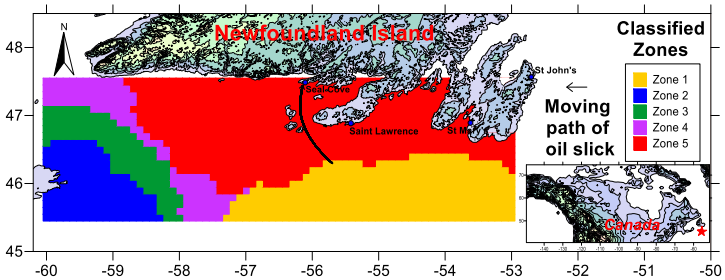






Response resources allocation/optimization
➔ Decision support systems (DSS)

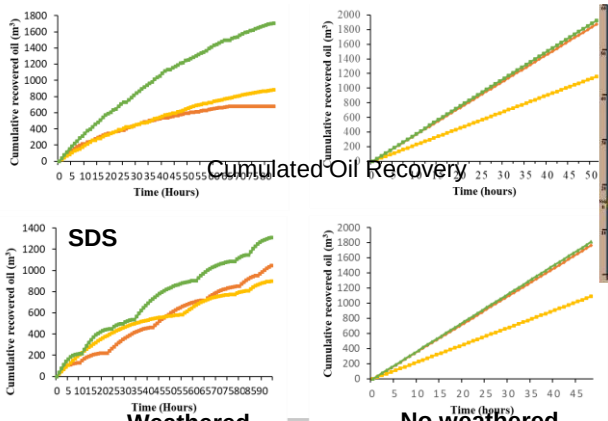


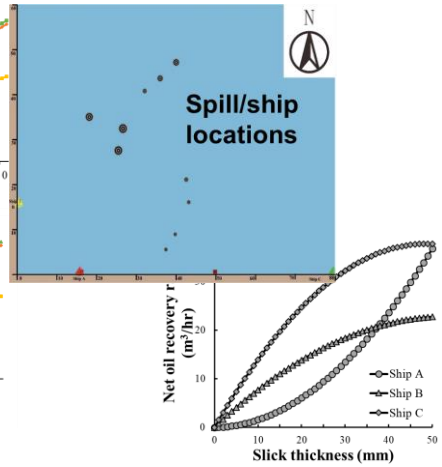


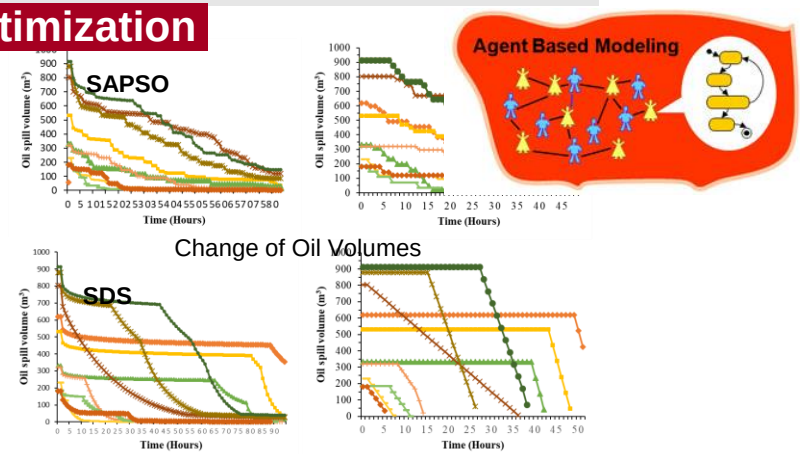
Spill vulnerability assessment & planning

5-2: AI aided optimization and human factor analysis

Emergency response decision making – AI aided optimization

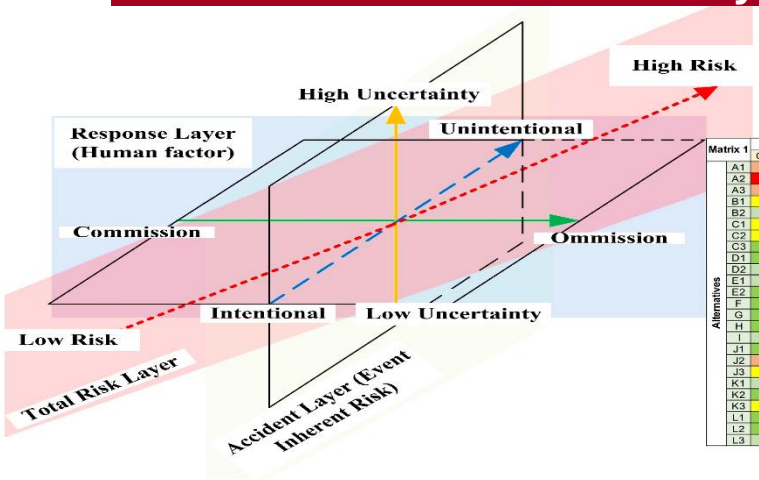


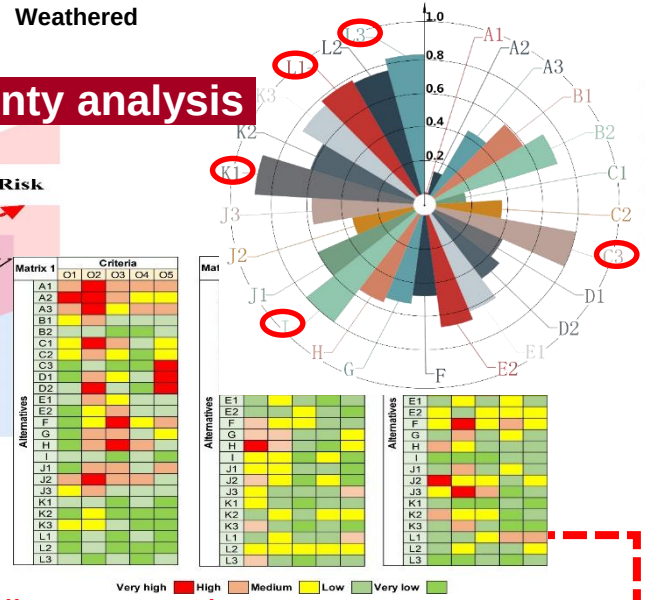




- **Top layer**
  - **Organizational Factor**
    - Government/company/ organizations
    - Decision/policy/standards/ response system/general procedures etc.
- **Median Layer**
  - **Group Factors**
    - Group leader management, supervision, crew, inspection, monitoring, maintenance, judgement, oversight, etc.
- **Low layer**
  - **Individual Factors**
    - Daily operation, response executor, personal behavior (physical and mental behaviors), etc.

Human factor & risk/uncertainty analysis





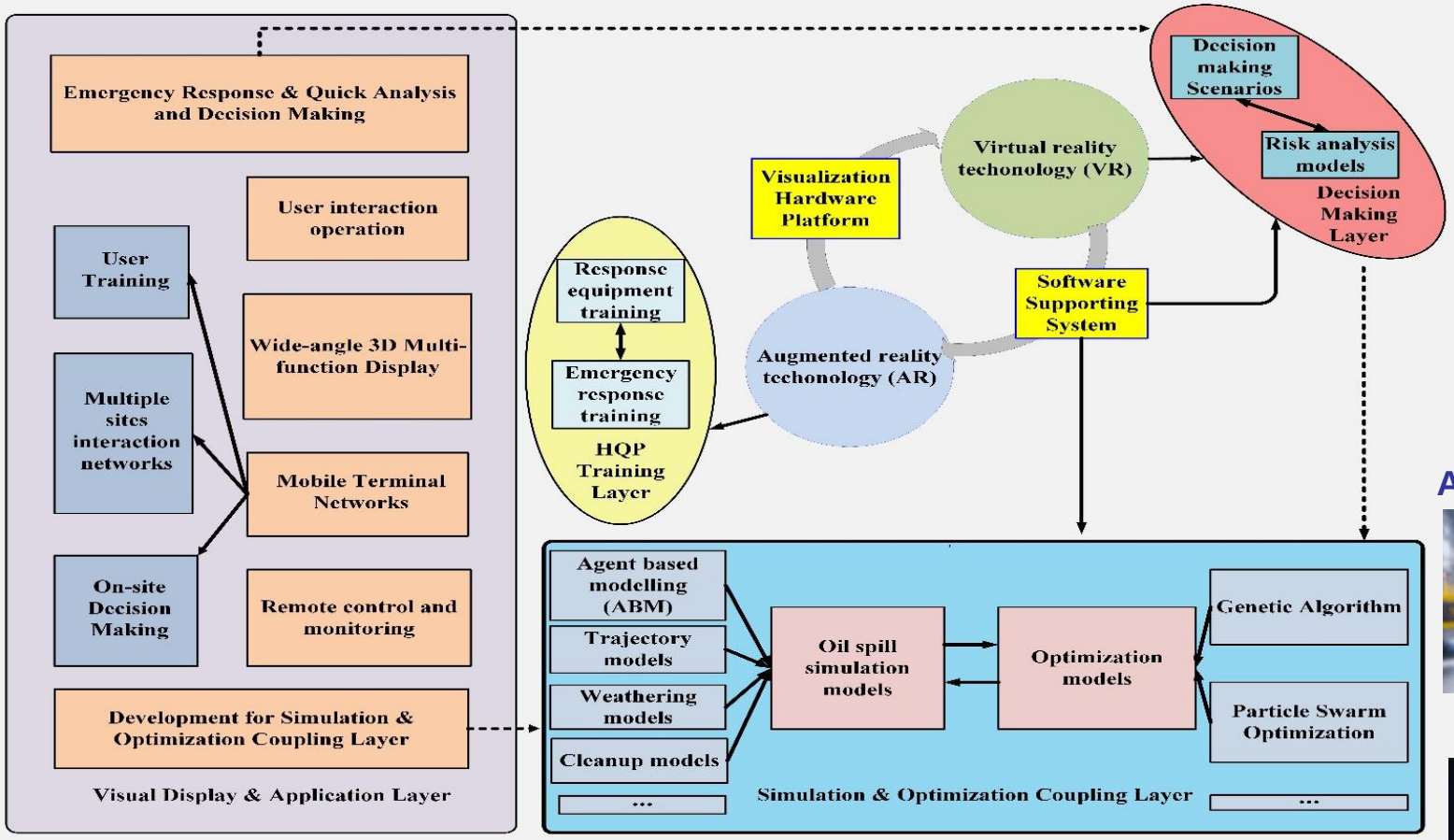
Research outputs:

1. Integrate artificial intelligence (AI) with simulation-optimization coupling approaches to support environmental modeling and decision making

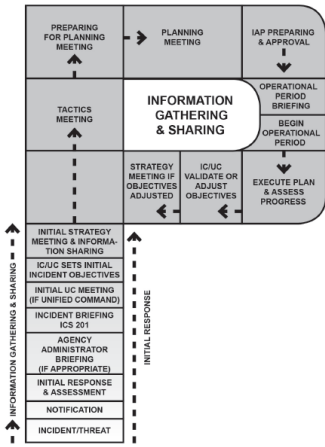
2. The first time to consider human factors and risk/uncertainty levels in a quantitative way during oil spill response decision making

5-3: AR/VR aided response training and decision making

vEER: Visualization Platform for Environmental Emergency Response Decision Support – Marine Oil Spill Response DSS



Pilot-scale Virtual Reality Modeling Platform for Offshore Oil SPill Response Decision Support



Augmented Reality

Virtual Reality

PEOPLE Network

Persistent, Emerging and Oil PoLlution in the Environment

"A pan-Canadian and global network"

Oil spills, POPs, and emerging contaminants
Marine & coastal environments; cold regions
➔ Engineering and Managerial SOLUTIONS!

- Detection, identification, and quantification
- Fate, behaviors, and transformation
- Prevention, control, and remediation
- Assessment, simulation, and decision making
- Ecotoxicological and socio-economic effect analysis
- Health and community impact and mitigation

- **Global cluster** of expertise and partnerships
- **Multidisciplinary research** and **tech transfer**
- **3-tier training strategy** - HQP, professionals and communities (esp. **Indigenous** People)
- **Evidence-based support** for stakeholders

✓ **180+ members incl. 130+ academic researchers & 150+ HQP from 21 Canadian & 13 intl institutions; 40+ Canadian partners incl. 7 fed., 4 prov./ municipal, 9 ind., 7 NGO etc. and international partners**

People create problems
PEOPLE find solutions

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INRS Institut national de la recherche scientifique · MUSC Medical University of South Carolina · NMBU Norwegian University of Life Sciences · SDU University of Southern Denmark · WARWICK THE UNIVERSITY OF WARWICK · UNITED NATIONS UNIVERSITY

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THE VISION OF BETTER TOMORROW

Cutting-edge R&D

Diverse Research Expertise

PEOPLE Network
Persistent and Emerging Organic Pollution in Environments

Multi-disciplinary Research Network

Technology Transfer

Our R&D goals/targets

Think and Do Outside the BOX!

Growing risk of oil spills gl d coastal environments ➔ **sustaina ?!**

- ❖ Accidental/chroni vater spills
- ❖ Intelligent plannin ing
- ❖ Human thinking a ponse
- ❖ Eco-frien ech
- ❖ Training c esearchers and responde
- ❖ plinary collaboration

Ne le and dedicated funding support

Acknowledgements

NRPOP LAB
Northern Region Persistent Organic Pollution Control Laboratory

PEOPLE Network
Persistent and Emerging Organic Pollution in Environments

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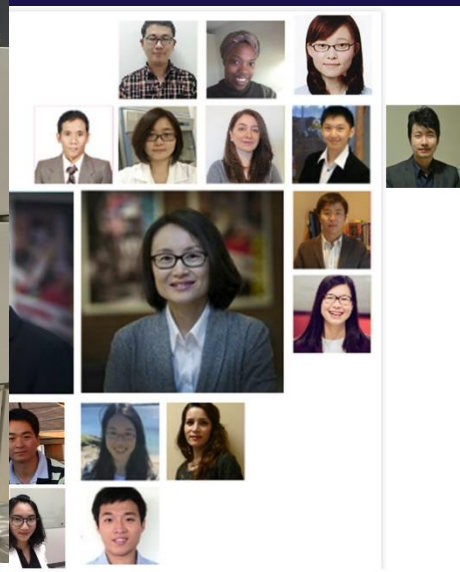
  Sunco
  ECRC
- Memo
  and other institutions
- Etc.



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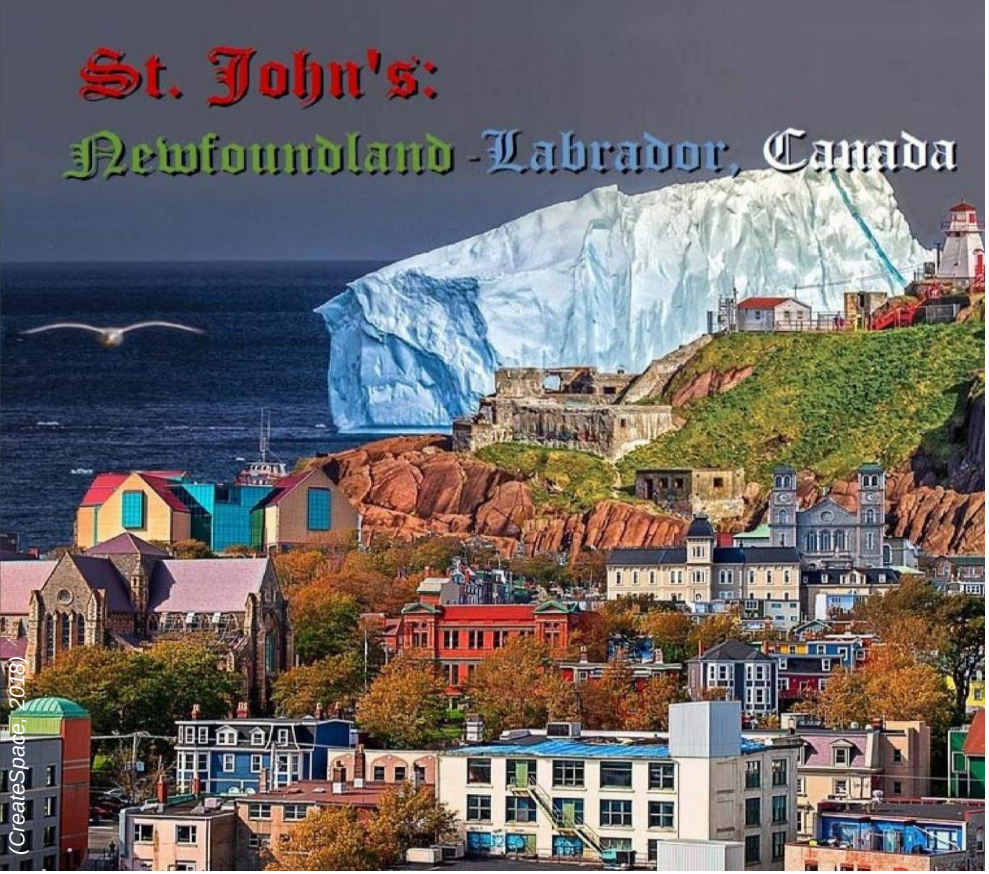

(CreateSpace, 2010)

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