

A STUDY TO CHARACTERIZE AND SOURCE HYDROCARBON CONTAMINATION OF SEDIMENTS AND SCALLOPS IN THE PORT AU PORT BAY, NL

PENNY MORRILL & MELISSA COOK
MEMORIAL UNIVERSITY
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1. Acknowledgements

The data presented in this report was collected and analysed by MSc student Melissa Cook as part of her thesis project. Logistical support was provided by the Port au Port Fishery Committee. We would like to especially thank Bill O’Gorman for his help as a field guide, as a captain, and as a diver. We would like to thank Lukas Kohl for volunteering to help collect field samples, and his help training Melissa in the lab with her extractions and processing her data; and Geert Van Biesen and Jamie Warren for their laboratory assistance. The work presented in this report was made possible by funding from the Harris Centre Applied Research Fund. Melissa Cook’s stipend was also partially supported by Memorial’s Graduate Baseline Funding Program, Dr. P. Morrill’s NSERC Discovery Grant, and a RDC Ocean Industry Student Research Award.

2. Executive Summary

In 2014, my research group was funded by the Harris Centre Applied Research Fund to characterize and contamination of sediments and scallops in the Port au Port Bay, NL. We worked with the local fish harvesters to locate and sample three types of sites: 1) the suspected source of petroleum hydrocarbon contamination in the bay (a site of former petroleum exploration wells where an oily substance is discharging into the bay), 2) fishing grounds in the bay, and 3) a non-contaminated site in the adjacent bay. Unfortunately, no live scallops were found in the fishing grounds. However, our aqueous geochemical measurements showed that there was no major inorganic contaminants in the waters of the fishing grounds. We returned to the site at the beginning of the scallop fishing season in 2015, where we were able to collect only one live scallop. The need for further research into the potential organic causes of scallop decline is demonstrated by the absence of scallops in 2014 and 2015 and the lack of inorganic contaminants in the water of the bay.

3. Introduction

3.1 Project Background

The local fish harvesters of the Port au Port area noticed an increase in the number of dead/empty scallops (also known as ‘clappers’) in the Fall of 2012. By 2013 almost all of the scallops in the area were clappers. For example, in one catch, 160 of 176 scallops were clappers (Gale, 2014). This problem has been limited to the Port au Port area including Fox Island, Shag Island, and Long Point and Shoal Point areas (Hillier, 2014). However, clappers are not a problem in nearby St. George (Fig. 1a). Scallops have been tested and determined to be free of disease. However, testing has not been performed to determine if organic or inorganic contamination could have been the cause in the collapse of the scallops’ fishery in the Port-au-Port area in 2013. In the Port au Port area alone there are typically 12 to 15 scallop draggers from July to December, and it is estimated that the loss of the scallops in this area will cost these individuals 25% of their income (Hillier, 2014). The Port au Port Fishery Committee asked for help to identify the cause and potential remediation of loss of their scallop fishery. The Port au Port Fishery Committee identified a number of potential causes including seismic testing, environmental contamination due to dumping and drilling, and climate change.

This report focuses on the potential inorganic and organic contamination. The Port au Port Fishery Committee has indentified an oily substance discharging into the bay in the vicinity of former petroleum exploration wells (Fig. 1b). Recent studies have found that oil and polycyclic hydrocarbons (PAHs) - a major component of crude oil - exposure affects scallop immune function with lethal and long-term results (Hannam et al., 2010a; Hannam et al., 2010b). If this study determines that these point sources of contamination have affected the scallops fishery, then environmental policy regarding prevention, and remediation should be put in place, not only for the Port au Port area, but other regions in NL as well.

3.2 Rationale

This study requested initial funds to collect and analyze a subset of samples to begin to identify and characterize the dissolved inorganic, dissolved organic, and hydrocarbon components of 1) the suspected source of petroleum hydrocarbon contamination in the bay, 2) fishing grounds in the bay, and 3) a non-contaminated site in the adjacent bay (i.e., George's Bay).

3.3 Objective(s)

The 1st Objective was to locate, map, and sample the 3 sites of interest 1) the suspected source of petroleum hydrocarbon contamination in the bay (a site of former petroleum exploration wells where an oily substance is discharging into the bay), 2) fishing grounds in the bay, and 3) a non-contaminated site in the adjacent bay. The 2nd Objective was to chemically characterize the 3 sites for total inorganic carbon (TIC), dissolved organic carbon (DOC), concentration so of dissolved inorganic ions such as metals, concentration of petroleum components (e.g. alkanes and PAHs). The 3rd Objective was to date sediments cores taken for each of the sites. The 4th Objective was to extract scallops for petroleum contaminants, and petroleum contamination metabolites. A subset of the scallop samples were to be analyzed for ¹⁴C content to determine the age of the carbon that they are metabolizing.

3.4 Research Methodology and Approach

To achieve Objective 1, *to locate, map, and sample the 3 sites of interest*, Melissa Cook teamed up with Port au Port Fishery Committee member Bill O'Gorman. Together Bill gave Melissa a tour of the Port au Port Bay. Melissa took notes and samples from: 1) the suspected source of petroleum hydrocarbon contamination in the bay, 2) the fishing grounds in the Port au Port Bay, and 3) a non-contaminated site in St. George's Bay (the adjacent bay).

To achieve Objective 2, *to geochemically characterize the petroleum source area, fishing ground(s), and an unaffected area*, Melissa filtered triplicate water samples for total inorganic carbon (TIC), dissolved organic carbon (DOC), and dissolved inorganic ions such as metals. All water samples were fixed to preserve the samples and kept cold and dark until analysis. Duplicate sediment cores were sampled at each site, and subdivided by depth. Sediment core sections were frozen. In the laboratory the core sections were freeze dried and extracted for petroleum components (e.g. alkanes and PAHs) following a modified versions of the EPA method 3540C, EPA method 3545, and Dionex application note 313. A new extraction method using new equipment acquired by the laboratory using NSERC RTI funding was tested against an older method. Additionally the new method was optimized for accuracy, reproducibility, and increased through put of samples. The methods were tested using an Environment Canada

Certified sediment standard for PAHs. Compound identification and quantification was performed using a gas chromatograph mass spectrometer (GC/MS).

To achieve Objective 3, *to date the sediment cores*, sediment cores for dating were taken alongside the sediment cores for organics. These cores were kept frozen. Sediment cores would be dated using ²¹⁰Pb to determine the age of each section and the sedimentation rates. For proper dating 12 to 15 samples were required per core.

To achieve Objective 4, *to extract scallops for indicators of petroleum contaminants*, scallops would be frozen flowing sampling, and freeze dried in the laboratory. The scallops would have been extracted and analyzed following a similar procedure described for the sediment core extraction method described above.

3.5 Clearances (ethics, biohazard, etc.)

No clearances were required. We were covered under the experimental license obtained by Memorial University of Newfoundland to harvest, collect, and sample shellfish for scientific, research, and educational purposes.

4. Project details and results

4.1 Locate, map, and sample hydrocarbon point-sources, fishing grounds, and unaffected area for scallops, sediment, and water

Initially Melissa Cook researched the history of drilling in the Port au Port area to identify wells drilled that could be leaking and contributing to hydrocarbon contamination in the Bay. Fig. 2 shows the recent and historic wells drilled in the area. Fig. 3 shows all of the sites sampled by Melissa Cook executed two field trips to the Port au Port region to collect samples: one at the end of the scallop fishing season in Oct. 2014 and one at the beginning of scallop fishing season in July 2015. Table 1 shows the number and type and location of samples taken.

Table 1. Sample list and location.

Analysis	Field Trip 1			Field Trip 2						
	Site 1	Site 2	Site 3	Site 1	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9
Ions	3	3	3	0	0	0	0	0	0	0
TIC	0	3	3	0	0	0	0	0	0	0
DOC	0	3	3	3	3	3	3	3	3	3
Sediment Cores*	0	2	2	2	2	2	2	2	2	2
Scallops	0	0	0	1	0	0	0	0	0	0

*Each sediment core was divided into 3 subsections of 2-3cm when collected

4.3 Chemically characterize contaminated and background samples

Water was sampled from a contaminated site (near Shoal Point), the scallop fishing grounds, and an uncontaminated site (in St. George's Bay). The water was then analyzed for inorganic ions, dissolved organic carbon (DOC), and total inorganic carbon (TIC).

A total of 37 different inorganic ions (e.g., Li, Be, B, Mg, Al, Si, P, S, Cl, Ca, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sn, Sb, I, Cs, La, Ce, Hg, Tl, Pb, Bi, and U) were analyzed for their concentrations. There were no obvious differences in the concentrations in the inorganic ions between the contaminated and the uncontaminated sites. This means that the waters near shoal point in the Port au Port Bay were similar in their inorganic ion concentrations to those of St. Georges Bay. The waters of the scallop fishing grounds were also similar. These data show that dissolved inorganic ions concentrations do not differ between the waters of St. Georges Bay, that is reportedly not having a problem with their scallop population, and the waters of Port au Port Bay.

Dissolved organic carbon (DOC) was measured for its concentrations and stable carbon isotope values in water sampled from Shoal Point, St. George's Bay, and a scallop fishing ground in Port au Port Bay. A difference was observed in the isotope values of the DOC sampled near Shoal point compared to St. George's Bay; that is to say that, the DOC at sampled from Shoal point had a more petroleum hydrocarbon signature. However, this signature was not observed in the waters sampled from the scallop fishing grounds. These data suggest that the impact of hydrocarbons on the dissolved organic carbon from the petroleum source site, is not observed in the dissolved organic carbon sampled from the fishing ground in Port au Port. A detailed map of hydrocarbon concentrations radiating from the petroleum source site into the Bay is required to determine the area extent of hydrocarbon contamination from the source site.

Total inorganic carbon (TIC) was measured for its concentrations and stable carbon isotope values in water sampled from Shoal Point, St. George's Bay, and a scallop fishing ground. The results of the TIC showed no evidence of petroleum hydrocarbons being oxidized.

4.4 Chemically characterized and date sediment cores

Unfortunately, the sediment cores collected were not long enough to get 12-15 samples from to date using Pb 210 dating. This bay either has very slow sedimentation rates, or it is periodically an erosional environment. However, there was enough sediment for chemical extraction of petroleum compounds. Our lab has recently received a new Accelerated Solvent Extractor (ASE). This equipment can automate the extraction of samples with the potential to increase extraction efficiency and reproducibility. When the method for extraction has been developed and tested, the equipment can extract as many samples in a day that the former (soxhlet) method can do in a month. Melissa Cook developed, tested and optimized a method for her solid samples using the ASE and a certified Environment Canada sediment standard for PAHs. Using her ASE method Melissa was able to increase her extraction efficiency, reproducibility, and her sample through put (Fig. 4). Using this method Melissa has extracted all of her sediment samples and she has submitted these samples for GC/MS analysis to the stable isotope laboratory in MUN's CREAT analytical facility. I have assurance from the laboratory manager that the samples will be run before the winter break.

4.5 Extract scallops and shells for petroleum contaminants, and petroleum contamination metabolites

There were two field trips to collect water, sediment, and scallop samples: one at the end of the scallop fishing season in Oct. 2014 and one at the beginning of scallop fishing season in July 2015. In total Melissa spent two weeks looking for scallops with the help of a local fisherman (Bill O'Gorman), but they only found one scallop. The lack of live scallops confirmed the continued decline of the scallops in the bay and the need for further research into the potential causes of this decline.

5. Recommendations on how this research should be implemented either as a public policy or a potential project as well as recommendations for future research)

The need for further research into the potential organic causes of scallop decline is demonstrated by the absence of scallops in 2014 and 2015 and the lack of inorganic contaminants in the water of the bay. A different approach, from what was used in this study, is needed to determine if petroleum hydrocarbons affected the scallops of Port au Port Bay, NL. First we need a detailed map of the distribution of hydrocarbons radiating from the suspected source of petroleum hydrocarbon contamination in the bay. Additionally, we need another way to determine if the health of scallops could have been affected by the petroleum hydrocarbons. We propose to do this by using other indicator organisms with similar feeding mechanisms and environmental niches (i.e., other more resilient molluscs).

6. Conclusion

In 2014, my research group was funded by the Harris Centre Applied Research Fund to characterize and source organic and inorganic contaminants of water, sediments, and scallops in the Port au Port Bay, NL. Melissa Cook developed and optimized a new method for solid extraction for alkanes and PAHs. We worked with the local fish harvesters to locate and sample three types of sites: 1) the suspected source of petroleum hydrocarbon contamination in the bay (a site of former petroleum exploration wells where an oily substance is discharging into the bay), 2) fishing grounds in the bay, and 3) a non-contaminated site in the adjacent bay (St. George's Bay).

Unfortunately, no live scallops were found in the fishing grounds. However, our aqueous geochemical measurements showed that there was no major inorganic contaminants in the waters of the fishing grounds. Our dissolved organic carbon samples did not show that the waters of the fishing grounds were impacted by the dissolved organic carbon of the petroleum hydrocarbon source site. However, the lack of scallops was still a problem. We returned to the site at the beginning of the scallop fishing season in 2015, where we were able to collect only one live scallop. Conclusions on the scallop decline cannot be based on one sample alone. The need for further research into the potential organic causes of scallop decline is demonstrated by the absence of scallops in 2014 and 2015 and the lack of inorganic contaminants in the water of the bay.

A different approach is needed to determine if petroleum hydrocarbons affected the scallops of Port au Port Bay, NL. First we need a detailed map of the distribution of hydrocarbons radiating from the suspected source of petroleum hydrocarbon contamination in the bay. We propose to do this using new environmental sensors developed by Memorial University (Drs. Bottaro and Hawboldt). Additionally, we need another way to determine if the health of scallops could have been affected by the petroleum hydrocarbons. We propose to do this by using other indicator organisms with similar feeding mechanisms and environmental niches (i.e., other more resilient molluscs).

7. References

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8. Figures

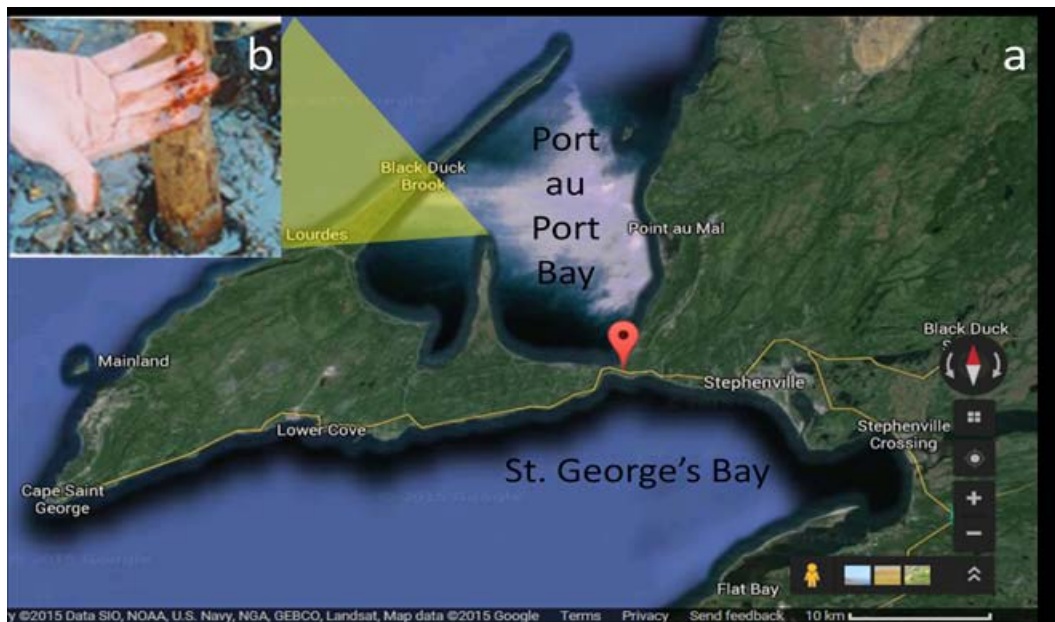


Figure 1. a. A Google map image of the Port au Port Bay and the St. George's Bay on the west coast of NL. **b.** The inset picture is of the oily substance discharging into the bay in the vicinity of former petroleum exploration wells. Image provided by the Port au Port Fishery Committee.

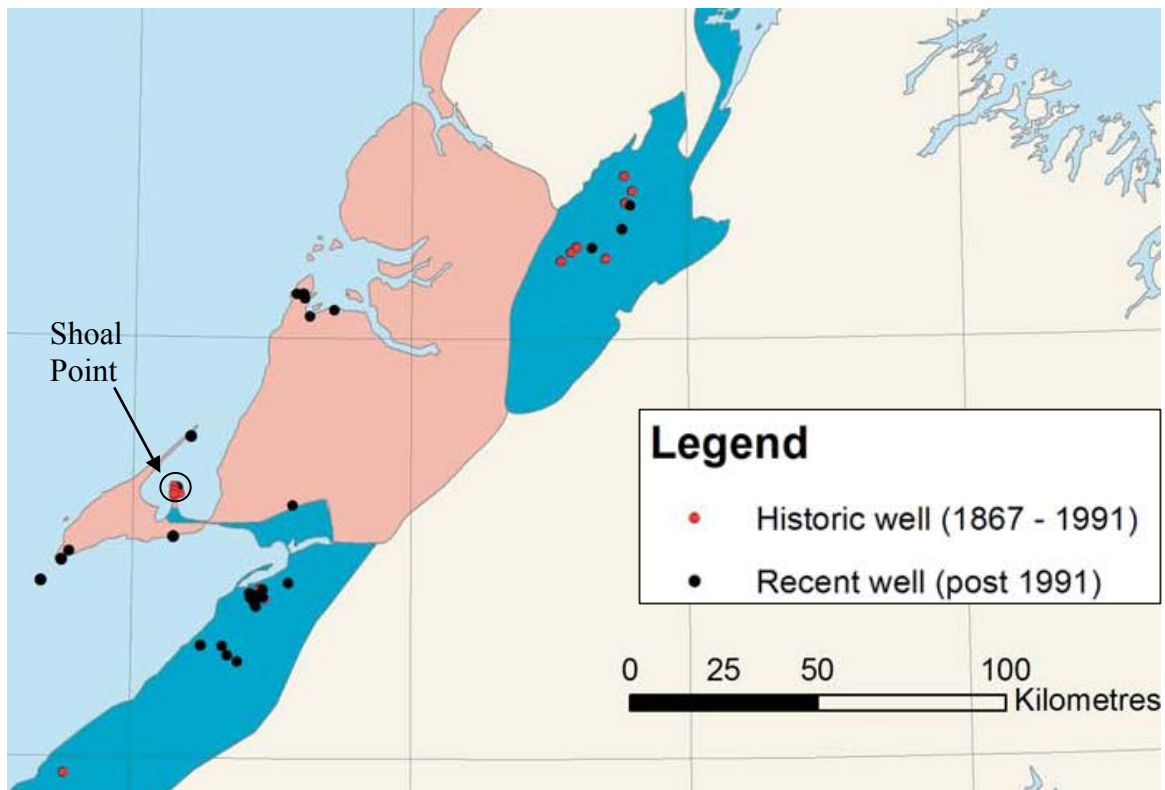


Figure 2. A map of recent and historic oil wells drilled the Port au Port area. The oily substance documented in Fig. 1a is coming from Shoal Point, and was the focus petroleum source area for this study.



Figure 3. Sample sites plotted a Google Earth Map.

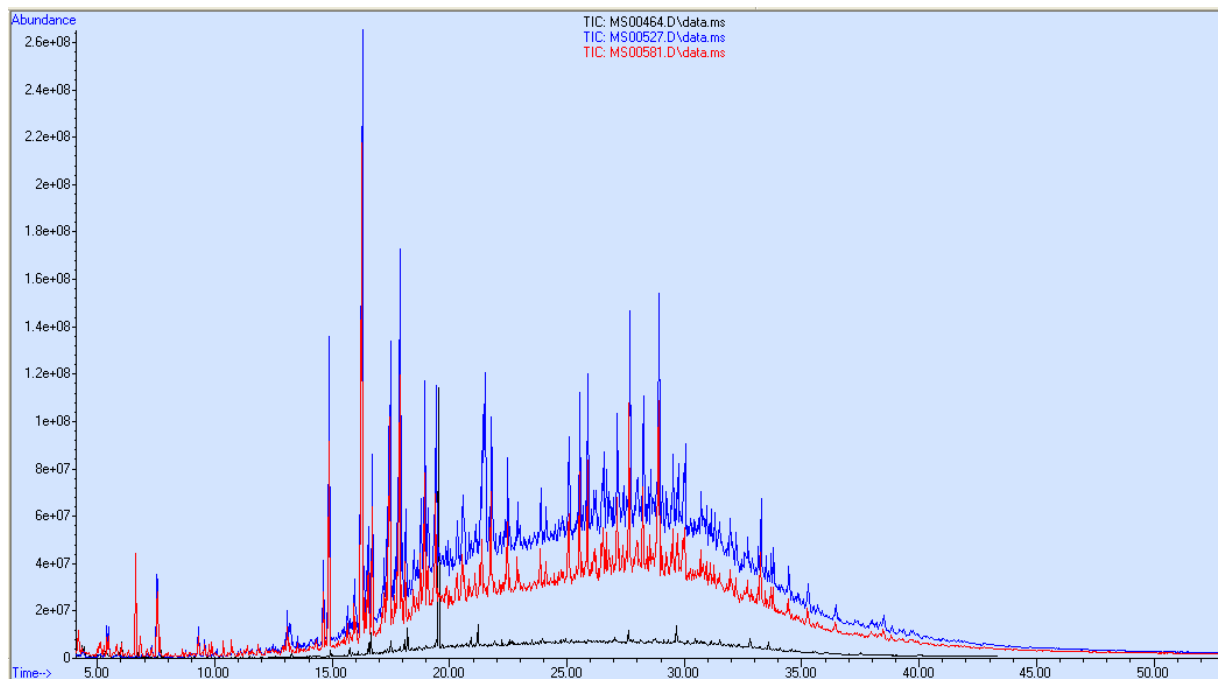


Figure 4. GC/MS chromatograms of ASE method development and optimization. The black line represents the PAHs that were extracted using the Soxhlet extraction method, the red line represents the PAHs that were extracted using the ASE method, and the blue line represents the PAHs that were extracted using the optimized ASE method.

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DOC	0	3	3	3	3	3	3	3	3	3
Sediment Cores*	0	2	2	2	2	2	2	2	2	2
Scallops	0	0	0	1	0	0	0	0	0	0

*Each sediment core was divided into 3 subsections of 2-3cm when collected

4.3 Chemically characterize contaminated and background samples

Water was sampled from a contaminated site (near Shoal Point), the scallop fishing grounds, and an uncontaminated site (in St. George's Bay). The water was then analyzed for inorganic ions, dissolved organic carbon (DOC), and total inorganic carbon (TIC).

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4.4 Chemically characterized and date sediment cores

Unfortunately, the sediment cores collected were not long enough to get 12-15 samples from to date using Pb 210 dating. This bay either has very slow sedimentation rates, or it is periodically an erosional environment. However, there was enough sediment for chemical extraction of petroleum compounds. Our lab has recently received a new Accelerated Solvent Extractor (ASE). This equipment can automate the extraction of samples with the potential to increase extraction efficiency and reproducibility. When the method for extraction has been developed and tested, the equipment can extract as many samples in a day that the former (soxhlet) method can do in a month. Melissa Cook developed, tested and optimized a method for her solid samples using the ASE and a certified Environment Canada sediment standard for PAHs. Using her ASE method Melissa was able to increase her extraction efficiency, reproducibility, and her sample through put (Fig. 4). Using this method Melissa has extracted all of her sediment samples and she has submitted these samples for GC/MS analysis to the stable isotope laboratory in MUN's CREAT analytical facility. I have assurance from the laboratory manager that the samples will be run before the winter break.

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There were two field trips to collect water, sediment, and scallop samples: one at the end of the scallop fishing season in Oct. 2014 and one at the beginning of scallop fishing season in July 2015. In total Melissa spent two weeks looking for scallops with the help of a local fisherman (Bill O'Gorman), but they only found one scallop. The lack of live scallops confirmed the continued decline of the scallops in the bay and the need for further research into the potential causes of this decline.

5. Recommendations on how this research should be implemented either as a public policy or a potential project as well as recommendations for future research)

The need for further research into the potential organic causes of scallop decline is demonstrated by the absence of scallops in 2014 and 2015 and the lack of inorganic contaminants in the water of the bay. A different approach, from what was used in this study, is needed to determine if petroleum hydrocarbons affected the scallops of Port au Port Bay, NL. First we need a detailed map of the distribution of hydrocarbons radiating from the suspected source of petroleum hydrocarbon contamination in the bay. Additionally, we need another way to determine if the health of scallops could have been affected by the petroleum hydrocarbons. We propose to do this by using other indicator organisms with similar feeding mechanisms and environmental niches (i.e., other more resilient molluscs).

6. Conclusion

In 2014, my research group was funded by the Harris Centre Applied Research Fund to characterize and source organic and inorganic contaminants of water, sediments, and scallops in the Port au Port Bay, NL. Melissa Cook developed and optimized a new method for solid extraction for alkanes and PAHs. We worked with the local fish harvesters to locate and sample three types of sites: 1) the suspected source of petroleum hydrocarbon contamination in the bay (a site of former petroleum exploration wells where an oily substance is discharging into the bay), 2) fishing grounds in the bay, and 3) a non-contaminated site in the adjacent bay (St. George's Bay).

Unfortunately, no live scallops were found in the fishing grounds. However, our aqueous geochemical measurements showed that there was no major inorganic contaminants in the waters of the fishing grounds. Our dissolved organic carbon samples did not show that the waters of the fishing grounds were impacted by the dissolved organic carbon of the petroleum hydrocarbon source site. However, the lack of scallops was still a problem. We returned to the site at the beginning of the scallop fishing season in 2015, where we were able to collect only one live scallop. Conclusions on the scallop decline cannot be based on one sample alone. The need for further research into the potential organic causes of scallop decline is demonstrated by the absence of scallops in 2014 and 2015 and the lack of inorganic contaminants in the water of the bay.

A different approach is needed to determine if petroleum hydrocarbons affected the scallops of Port au Port Bay, NL. First we need a detailed map of the distribution of hydrocarbons radiating from the suspected source of petroleum hydrocarbon contamination in the bay. We propose to do this using new environmental sensors developed by Memorial University (Drs. Bottaro and Hawboldt). Additionally, we need another way to determine if the health of scallops could have been affected by the petroleum hydrocarbons. We propose to do this by using other indicator organisms with similar feeding mechanisms and environmental niches (i.e., other more resilient molluscs).

7. References

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8. Figures

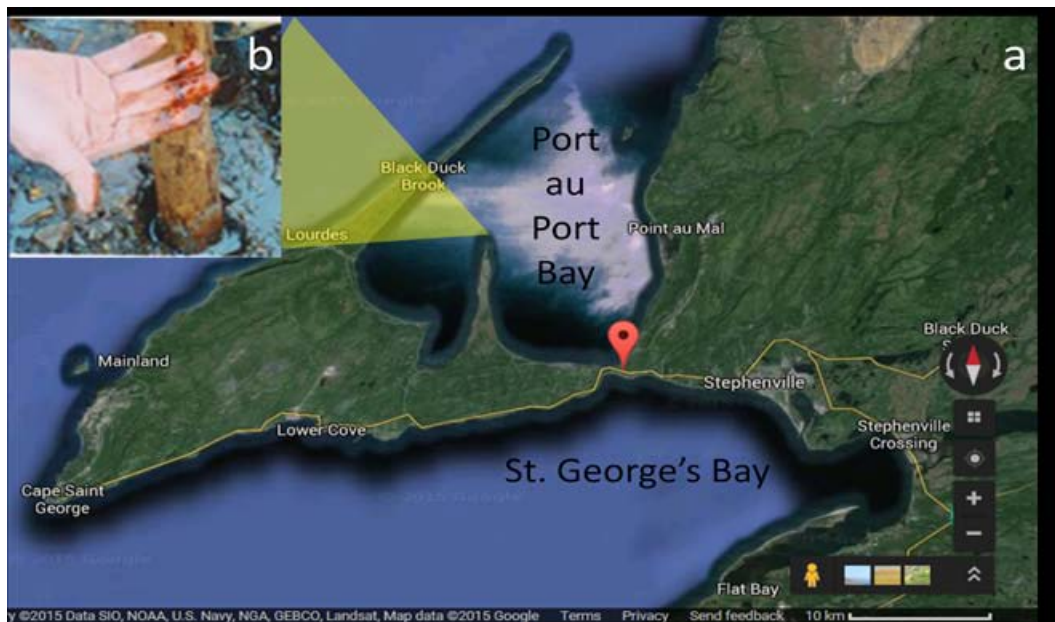


Figure 1. a. A Google map image of the Port au Port Bay and the St. George's Bay on the west coast of NL. **b.** The inset picture is of the oily substance discharging into the bay in the vicinity of former petroleum exploration wells. Image provided by the Port au Port Fishery Committee.

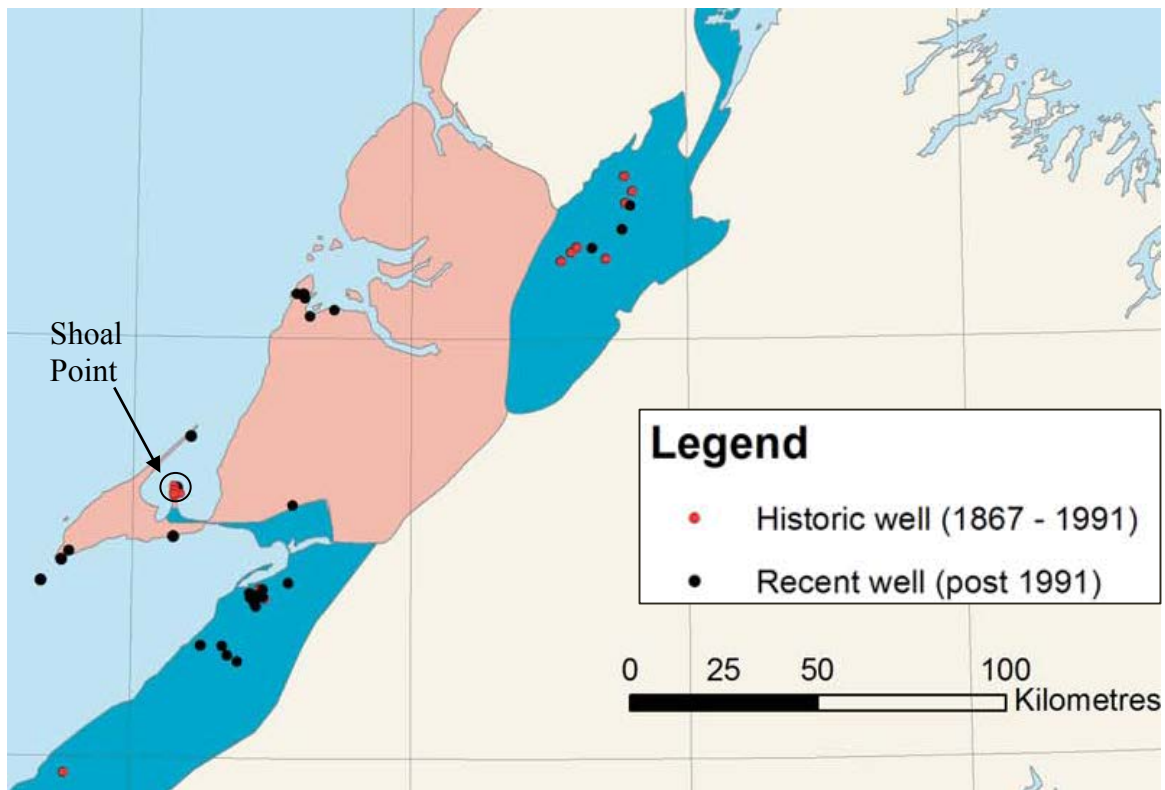


Figure 2. A map of recent and historic oil wells drilled the Port au Port area. The oily substance documented in Fig. 1a is coming from Shoal Point, and was the focus petroleum source area for this study.



Figure 3. Sample sites plotted a Google Earth Map.

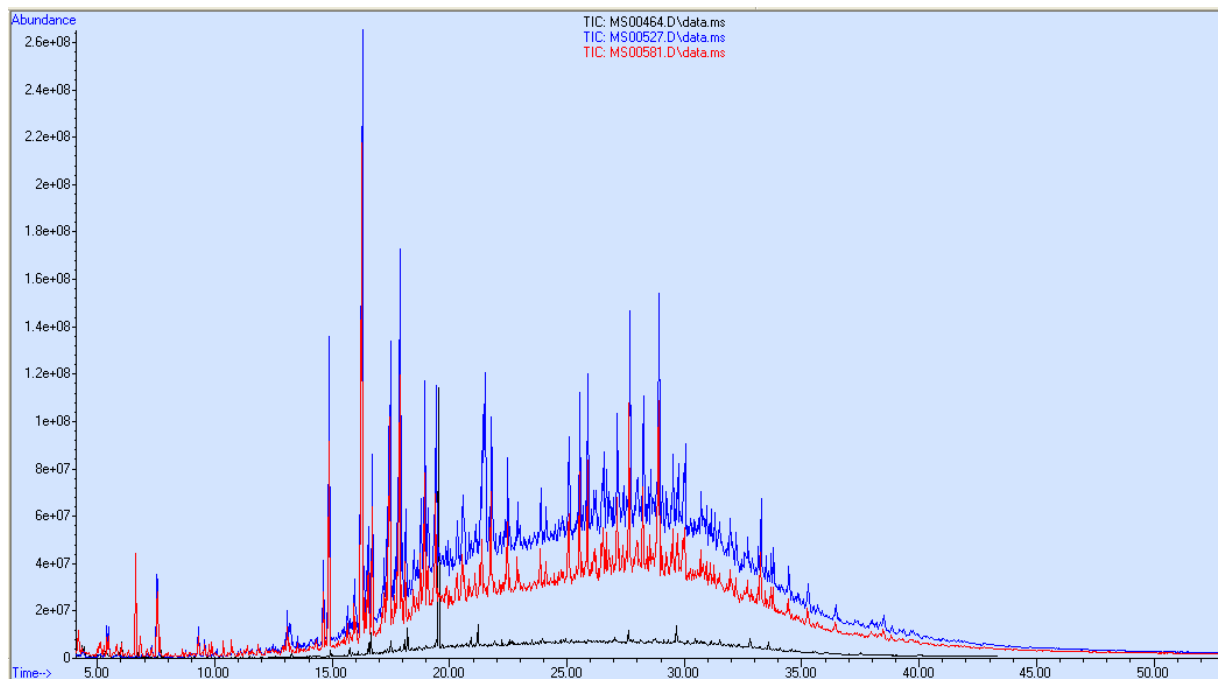


Figure 4. GC/MS chromatographs of ASE method development and optimization. The black line represents the PAHs that were extracted using the Soxhlet extraction method, the red line represents the PAHs that were extracted using the ASE method, and the blue line represents the PAHs that were extracted using the optimized ASE method.