# CHARACTERIZATION AND EVALUATION OF POTENTIAL CONTAMINANTS OF CONCERN IN SMALL CRAFT HARBOUR SEDIMENTS IN NOVA SCOTIA

by

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## ABSTRACT

Small craft harbours (SCHs) are vital for the fishing industry, but can be impacted by contamination in marine sediments. This study characterized the distribution of petroleum hydrocarbons (PHCs) and polychlorinated biphenyls (PCBs) in 31 SCHs sediments in Nova Scotia between 2000 and 2017. Federal and regional sediment quality guidelines were used to determine exceedances. An ecological risk evaluation for PHCs, PCBs and previously characterized contaminants was also conducted using two different approaches. While results showed exceedances for heavy PHCs, only 7% of samples exceeded maximum recommended screening level, showing low risk. PCBs did not pose high risk to biota, with only six samples exceeding the higher effect level. Most SCHs showed low ecological risk, with two SCHs presenting high risk. Monitoring is recommended for high risk SCHs to determine extent of contamination. Integrated results inform harbour managers about the historical state of SCHs, so future risk-management options can be developed.

## LIST OF ABBREVIATIONS USED

| | |
|---|---|
| ANOVA | Analysis of variance |
| As | Arsenic |
| Atlantic RBCA | Atlantic Risk-Based Corrective Action |
| Atlantic PIRI | Atlantic Partnership in Risk-Based Corrective Action Implementation |
| BTEX | Benzene, toluene, ethylbenzene and xylenes |
| CALA | Canadian Association for Laboratory Accreditation |
| CCME | Canadian Council of the Ministers of the Environment |
| Cd | Cadmium |
| CEPA | *Canadian Environmental Protection Act* |
| CoC | Contaminants of concern |
| Cr | Chromium |
| Cu | Copper |
| DFO | Fisheries and Oceans Canada |
| ECCC | Environment and Climate Change Canada |
| ERA | Ecological risk assessment |
| $F_{oc}$ | Fraction organic carbon |
| Hg | Mercury |
| ISQGs | Interim Sediment Quality Guidelines |
| $K_{oc}$ | Organic carbon-water partitioning coefficient |
| $K_{ow}$ | Octanol-water partition coefficient |
| Modified TPH (Gas) | Hydrocarbons with 6 to 10 carbon atoms (C6-C10) |
| Modified TPH (Fuel) | Hydrocarbons with 10 to 21 carbon atoms (C10-C21) |
| Modified TPH (Lube) | Hydrocarbons with 21 to 32 carbon atoms (C21-C32) |
| mPEL-Q | Mean probable effect level quotient |
| MSSP | Marine Sediment Sampling Program |
| Ni | Nickel |
| PAHs | Polycyclic aromatic hydrocarbons |
| Pb | Lead |
| PCBs | Polychlorinated biphenyls |
| PELs | Probable Effect Levels |
| PHCs | Petroleum hydrocarbons |
| PHC CWS | Canada-Wide Standards for Petroleum Hydrocarbons |
| PSPC | Public Services and Procurement Canada |
| POPs | Persistent Organic Pollutants |
| RDLs | Reportable detection limits |
| SCC | Standards Council of Canada |
| SCHs | Small craft harbours |
| SQGs | Sediment quality guidelines |
| TOC | Total organic carbon |
| TPH | Total petroleum hydrocarbons |
| USEPA | United States Environmental Protection Agency |
| Zn | Zinc |

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# CHAPTER 1 INTRODUCTION

## 1.1 Sediment contamination in marine harbours

Marine sediments have high ecological importance. They are species-rich systems that serve as habitat for several epifaunal and infaunal populations, and influence the environmental fate of several pollutants in marine ecosystems (Snelgrove, 2013; Yang, 2018). They have a wide composition range, such as clay, silt, sand, gravel, decaying organic matter, and shells among other things. Sediments also function as a source of nutrients and energy in aquatic food webs, while supporting various biogeochemical processes (Krumins et al., 2013; Wall et al., 2010). Given that particulate matter precipitates into the ocean floor, sediments tend to collect and accumulate contaminants, particularly fine grain sediments. Additionally, hydrophobic contaminants can strongly bind to marine sediments, causing sediments to act as long-term pollution sources even after the original source is not present anymore (Luthy, 2004). Globally, the main sources of contamination for marine harbours include land runoff, industrial activities emissions, spills, and leaks from inadequate storage, anti-foulant paints, ship repairs and buildings, loading and bunkering operations and dry-docking activities (World harbour project, 2016). The most common contaminants present in coastal areas with large anthropogenic presence, such as ports and harbours, are pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), heavy metals and petroleum hydrocarbons (PHCs) (Dell'Anno et al., 2021; USEPA, 2022b).

## 1.2 Small craft harbour (SCH) program

Harbours and ports are vital pieces of infrastructure as they have crucial contributions to the economy and transportation of communities worldwide (USEPA, 2022a). They also are socio-culturally important by providing means of livelihood, recreation, and sense of belonging to surrounding residents (Pearson et al., 2016). In Canada, small craft harbours (SCHs) are a classification established by Fisheries and Oceans Canada (DFO) for small-scale but significant harbours. The SCH program run by DFO oversees the operation and maintenance of SCHs so they can be used by the commercial fishing industry and other

users (DFO, 2021). As of September 2018, this program manages 1008 harbours nationally, for fishing (87.5%) and recreational activities (12.5%). In total, these harbours are valued at approximately $5.6 billion CAD (DFO, 2019).

One of the provinces where SCHs are a crucial part of economic activities is Nova Scotia. They are culturally important and crucial to connect local commercial fisheries to the global economy (Ragan, 2021). In 2016, the 178 fishing SCHs found in Nova Scotia accounted for 58.9% ($3.3 billion CAD) of the national infrastructure value for SCHs (Fig. 1.1; DFO, 2016; Davis et al., 2018). However, SCHs often face management challenges and can become dumping sites for transient and local users, leading to contamination (Meloche and McDonald, 2018). Some SCHs can also have an uncertain usage history and are located close to other contamination sources like bulk plants or ferry terminals (Kettlewell and Guest, 2014). These conditions lead to the release of substances that could potentially contaminate surrounding soil, water, and sediments. Contamination in SCHs can have impacts on humans and biota.

**Figure 1.1** Fishing boats at Clark's Harbour, Nova Scotia (Jarvis, 2008).

### 1.3 Potential contaminants of concern (CoC) in SCHs sediments

Contamination sources and potential contaminants of concern (CoC) in SCHs are consistent with trends observed in harbours and ports globally. DFO (2012) identified paints and antifoulants, oily bilge water, fuel spills and fish waste as common pollution sources in SCHs, and emphasized how these substances can affect marine environments and fisheries. Industrial sites near SCHs, such as fish plants, aquaculture facilities, and wood and timber activities, can also act as sources of contaminants such as PCBs, pesticides or antibiotics. Prevalent contamination issues include waste disposal in the intertidal and subtidal zones, runoff from solvents, paint and metals used during boat maintenance, creosote-treated piling that contribute to PAH contamination in a waterlot, among others (Meloche and McDonald, 2018).

During a risk management study for SCHs in British Columbia, Meloche and McDonald (2018) created a conceptual site model (Fig. 1.2). It identified the main sources, pathways, contaminants, and receptors interacting within a SCH. While this assessment focused on SCHs in the Canadian west coast, most conditions and activities conducted in the Canadian east coast are comparable. Thus, similar potential CoC could be expected in SCHs in Nova Scotia. However, it is worth noting that the conceptual site model is only used as an example of potential sources of contamination in SCHs and does not represent the actual conditions of SCHs in Nova Scotia. It is important to characterize and assess potential CoC to understand the historical and current state of SCHs, identify sources of prior and ongoing contamination and determine if clean up or remediations actions are needed.

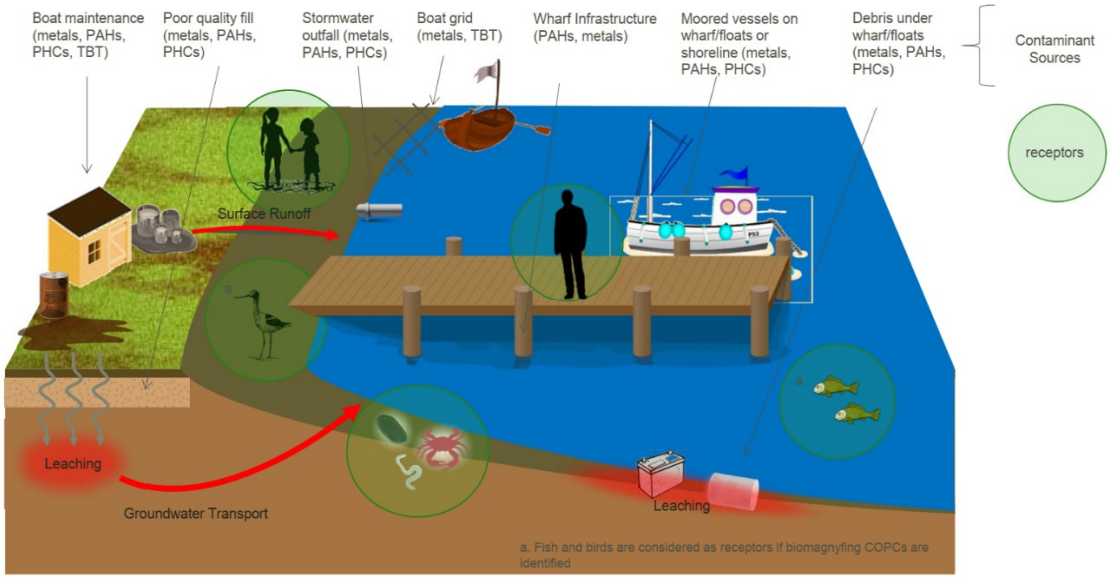


**Figure 1.2** Example of a conceptual site model for a small craft harbour (Meloche and McDonald, 2018).

## 1.4 Research scope

This thesis focused on SCHs in Nova Scotia, Canada, and built on previous research conducted in the same study area. Of the 178 SCHs in the province, 31 SCHs were selected to conduct this research (Table, 1.1; Fig. 1.3). The sequence and classification by region of the chosen SCHs is described in Chapter II and the methods section of Chapters III and Chapter IV. SCH selection derives from an assessment conducted by Walker et al. (2013) to identify cost effective sediment dredge disposal options for priority SCHs in Nova Scotia. Previous studies have characterized PAHs and metal contaminants in sediments from these selected SCHs (Davis et al., 2018; Davis et al., 2019a; Davis et al., 2019b; Zhang et al., 2019a; Zhang et al., 2019b). For research continuity and to compare to existing data, this study used the same 31 SCHs. As for potential CoC to analyze, the thesis scope was to characterize PHCs and total PCBs. Characterizations carried out for PAHs (Davis et al., 2018) and metals (Zhang et al., 2019a) were used as complementary data for the second part of the research – the ecological risk evaluation. While other CoC may be present in the study area, three of the classes of contaminants selected for this thesis align with the main potential CoC identified in the conceptual site model by Meloche and McDonald (2018).

**Table 1.1** Selected SCHs classified by region and identified sequentially.

| Eastern Nova Scotia | Gulf Nova Scotia | Southwest Nova Scotia |
|---|---|---|
| 1. Canso<br>2. Glace Bay<br>3. Neil's Harbour<br>4. Owls Head<br>5. Port Morien<br>6. Three Fathom Harbour | 7. Arisaig<br>8. Bailey Brook<br>9. Barrios Beach Tracadie<br>10. Caribou Ferry<br>11. Inverness<br>12. Judique Baxter's Cove<br>13. Pictou Landing<br>14. Pleasant Bay<br>15. Skinners Cove | 16. Battery Point<br>17. Centreville<br>18. Clark's Harbour<br>19. Delap's Cove<br>20. Fox Point<br>21. Hampton<br>22. Hunts Point<br>23. Little Harbour Shelburne<br>24. Little River Yarmouth<br>25. Moose Harbour<br>26. Pinkney's Point<br>27. Sandford<br>28. South Side<br>29. Stoney Island<br>30. Westport<br>31. Yarmouth Bar |

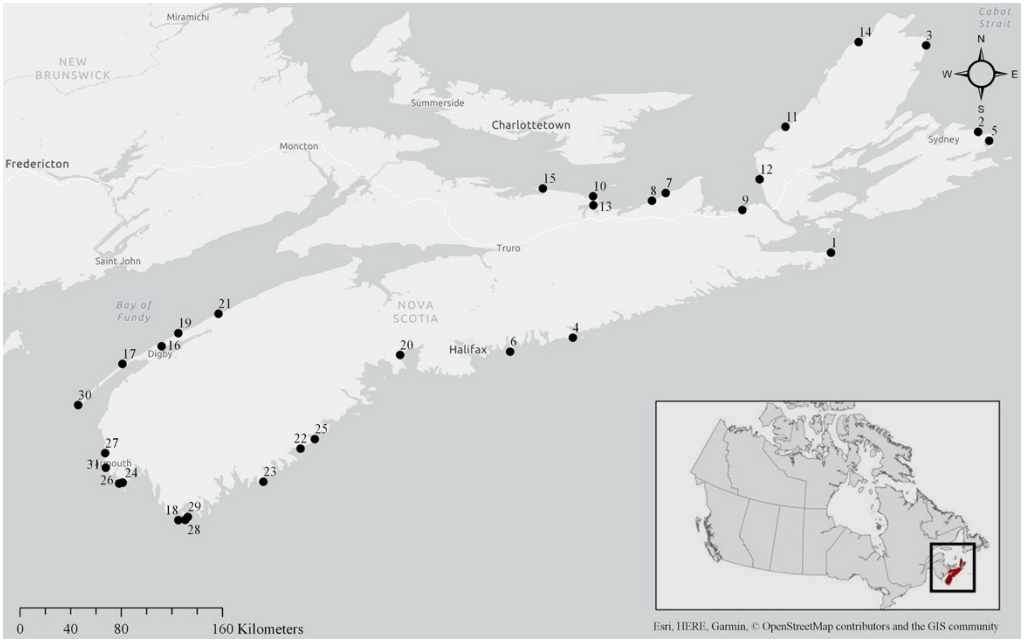


**Figure 1.3** Selected SCH locations in Nova Scotia [Inset map of Canada was produced by DMTI™].

## 1.5 Research objectives

This thesis aims to provide a historical overview of potential CoC concentrations in SCHs sediments in Nova Scotia and to integrate my own and prior research in the area to conduct an ecological risk evaluation. Specifically, the main objectives of this research were to:

1. Spatiotemporally identify the abundance and distribution of PHCs and total PCBs in SCHs sediments across Nova Scotia;
2. Evaluate the potential ecological risk posed by the interaction of multiple contaminants in SCHs sediments in Nova Scotia; and,
3. Determine if there are SCHs classified as high priority for immediate clean-up action and present potential management recommendations for these sites.

### 1.6 Methodology

This study used secondary data collected by DFO through their Marine Sediment Sampling Program (MSSP). These reports contained results from sediment samples collected between 2000 and 2017 from the 31 SCHs. To complete the first objective, PHC and total PCB concentrations of sediment samples were collected, standardized and compared to federal and regional sediment quality guidelines (SQGs) – Atlantic Risk Based Corrective Action (Atlantic RBCA), Canadian SQGs for the Protection of Aquatic Life and *Canadian Environmental Protection Act* (CEPA) Disposal at Sea guidelines – to determine exceedances. For the second objective, PAH and metal data were gathered from previous studies and integrated with the results from the first objective. An ecological risk evaluation was conducted using two lines of evidence: mean probable effect level quotients (mPEL-Q) and number and frequency of SGQs exceedances. For the last objective, results from both methodologies were complied and analyzed to make appropriate recommendations for future SCH actions.

### 1.7 Thesis layout

This thesis is structured in a manuscript-based manner. Chapter 3 and 4 are presented as stand-alone journal articles with their own abstracts, introductions, methods, results, discussion and conclusions. The first manuscript has been accepted and is awaiting publication, while the second one is under journal revision. Because of this layout, some repetition may occur between chapters. After a brief introduction in Chapter 1, Chapter 2 presents background information and a literature review on the research subject matters. Chapter 3 is the first manuscript, focused on the spatiotemporal characterization of PHCs

and total PCBs in SCHs sediments in Nova Scotia. Chapter 5 is the second manuscript, discussing the multi-contaminant ecological risk evaluation. Lastly, Chapter 5 presents the overall conclusion of the research, key findings and provides recommendations on future actions in the study area. References, grouped by chapters, are presented at the end of the thesis.

# CHAPTER 2 BACKGROUND

## 2.1 Small craft harbours (SCHs)

### *2.1.1 SCHs nationwide*

Small craft harbours (SCHs) is a Canadian program created in 1977 under the authority of the Fishing and Recreational Harbours Act, and is being currently managed by Fisheries and Oceans Canada (DFO) (Fishing and Recreational Harbours Act, 1985). They are critical to the commercial fishing industry, since nearly 90% of the Canadian fish harvests are landed at a designated SCH (DFO, 2013). SCHs are estimated to provide employment to approximately 45,000 people throughout Canada when providing support to the commercial fisheries, whose landings were valued at approximately $3.7 billion CAD in 2019 (DFO, 2021a). SCHs also provide services to a range of different users like Indigenous fishers, aquaculturists and water taxis, among others. The main objective of the SCHs program is to guarantee that fishing harbours are maintained in good conditions and operational (DFO 2014; DFO, 2021b). SCHs are classified as core and non-core. Core fishing harbours are defined as those crucial to the aquaculture and fishing industries, which are owned and managed by the DFO harbour authorities. (DFO, 2019). Non-core SCHs are recreational harbours or low-activity fishing that have been divested to municipalities or local communities (DFO, 2014). DFO oversees providing the necessary environmental cleanup and repairs before transferring a SCH to a third party (DFO, 2019).

Harbour authorities at SCHs are required to follow contamination prevention requirements to reduce the adverse effects of harbour operations on the marine environments (DFO, 2012). SCHs can be potentially contaminated since they are used by a wide variety of people. They can also be located near in-land contamination sources like bulk plants (Kettlewell and Guest, 2014). Because of their constant use by multiple types of users and activities surrounding the area, SCHs can have presence of pollutants. Furthermore, some SCHs may be located in remote communities where adequate harbour management can be challenging (McManus and Hamilton, 2019). In 2019, a report focused on the sustainability of SCHs determined that appropriate resources should be

allocated to the SCHs program to maintain functional SCH infrastructure (Standing Committee on Fisheries and Oceans, 2019). On their recommendations, the committee emphasized the need to increase the budget available for the SCH program given the impact of climate change (e.g., severity of storms and sea level rise damaging vessels and SCH infrastructure), accelerating degradation of facilities and growing demand, as well as bringing data on SCH conditions and performance to date. They also recommended to prioritize capital and repair projects based on health and safety risks to SCH users (Standing Committee on Fisheries and Oceans, 2019; DFO, 2021a). In 2021, DFO announced an investment of $300 million CAD for repairments, renewals and replacement activities of the Canadian SCH network (DFO, 2021a).

### *2.1.2 SCHs in Nova Scotia*

SCHs are quite important in Nova Scotia. It is estimated that just three SCH in the Digby Neck area provide hundreds of jobs for surrounding communities and account for up to $60 million of economic impact in the region (Standing Committee on Fisheries and Oceans, 2019). Nova Scotia has three SCH management regions established by DFO – Eastern Nova Scotia, Gulf Nova Scotia and Southwest Nova Scotia. (Fig. 2.1).

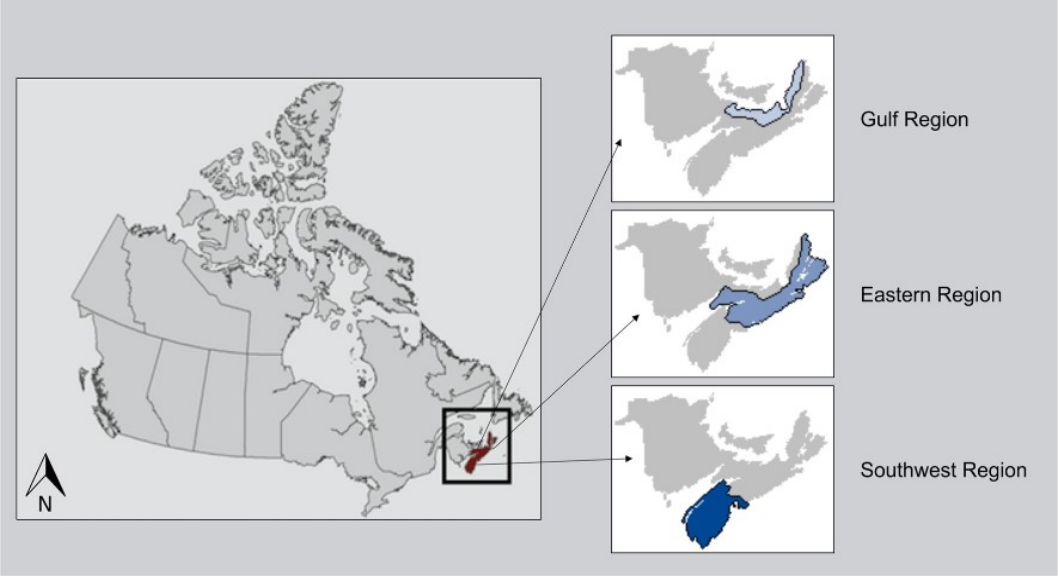


**Figure 2.1** DFO SCHs management regions in Nova Scotia (Davis et al., 2018; DFO,2019b).

DFO (2018) defines each region as follows: Eastern Nova Scotia encompasses the Nova Scotia coast of the inner Bay of Fundy, the eastern part of Cape Breton and the eastern half of the south shore of Nova Scotia. SCHs in the Bay of Fundy operate all year round, while the rest of the SCHs in the region close during winter. Most of them are comprised are used for inshore fishing through small-scale vessels (less than 45 feet). The Gulf region includes the Nova Scotia southern coast of the Gulf of St. Lawrence, from the northern tip of Cape Breton to the New Brunswick border. Cheticamp is the largest SCH, used by bigger vessels for mid-shore fishing of herring and snow crab. Other significant inshore fisheries are carried out in this region, including lobster. SCHs are locked in by ice in the winter and therefore closed. Southwest Nova Scotia covers the southwestern half of Nova Scotia. This region has two different shorelines, both being ice-free the majority of the year and having rocky coastlines: the Atlantic Ocean with moderate tides and high tides (up to 10 meters) in the Bay of Fundy. SCHs are operational throughout the year, supporting both in and mid-shore fisheries like scallop, herring, groundfish and lobster.

Previous research in SCHs in Nova Scotia has shown that some SCHs presented PAHs concentrations that would cause negative health affects or toxicity impacts to biota, based on the thresholds established in sediment quality guidelines (SQGs). While SQGs do not always represent a line beyond which you will experience toxicity, they provide an adequate point of reference for initial studies in an area. SCHs in the Southwest region of Nova Scotia were found to be the most impacted. Additionally, distribution of individual PAHs in sediments followed global distribution trends in similar environments (Davis et al., 2018). As for PAH potential sources, SCHs sediments were most impacted by combustion sources, likely associated to coal combustion, biomass incineration and vehicular emissions in Nova Scotia. Activities specifically related to harbours such as fuel spills or boat traffic contributed to PAHs in sediments to a much lesser extent. (Davis et al., 2019a). More than 56% of the metal contaminant samples were below low effect level and more than 96% were below SQGs high effect levels, indicating a low likelihood of adverse effects for marine biota (Zhang et al., 2019a). Zhang et al. (2019b) identified a significant variation in metals distribution throughout SCHs, which could be attributed to

dredging activities in the harbour that inhibit long-term buildup in the sediments. Based on a single-contaminant ERA, most SCHs showed low ecological risks from sediment metal concentrations. However, two SCHs (Canso in the Eastern region and Clark's Harbour in the Southwest region) had the highest metal contamination with a moderate ecological risk (Zhang et al., 2019b).

Marine underwater benthic habitat surveys have also been conducted at various SCHs in Nova Scotia. A survey carried out by CBCL Limited (2016) in Auld's Cove in the Gulf region showed that slow moving and sessile macrofauna were the most abundant, while highly motile macrofauna diversity and abundance was relatively low in comparison. Species such as rock crabs, northern sea stars, hermit crabs, American oysters and blue mussels were found in the area. A similar study conducted by Stantec (2019a) in Caribou Ferry and Pictou Landing (Gulf region) also indicated the presence of the same species as Auld's Cove, as well as holes of different sizes in the sediment for infauna, though no infauna species were observed in the video. Macroflora was sparse in both studies, with only certain species of algae found throughout the study areas. In a regional context, benthic invertebrate communities were also monitored around Sydney Harbour between 2009-2011 as part of the Sydney Tar Ponds Cleanup and Coke Ovens Remediation Project (Stewart et al., 2016).

For social science research, data from Nova Scotia SCHs were found to be aligned with findings and recommendations from the Standing Committee on Fisheries and Oceans (2019). Through interviews and media analysis, Ragan (2021) identified that funding and climate change were the most significant threats to livelihood relying on SCHs. Some participants also mentioned that divesting SCHs has impacted their communities. Because maintenance was not as thorough as before, SCHs were not considered safe anymore and users moved to other facilities (Ragan, 2021). Walker et al. (2015a) projected potential issues when divesting SCHs in Nova Scotia such as the inability to upkeep existing management protocols. New SCH authorities may lack the financial and technical resources to continue with existing procedures and to fully understand historical contamination on a site. Training, education and awareness policies when transferring

SCHs can help ensure adherence to protocols and effective management of environmental liabilities (Walker et al., 2015a).

### 2.2 Marine sediment sampling program (MSSP)

Sediment quality in SCHs is monitored by DFO through their marine sediment sampling program (MSSP). The purpose of MSSPs is to sample and characterize sediment quality from SCHs and to determine disposal options if sediment will be dredged from a site (Amec Foster Wheeler, 2015; Stantec, 2019b).

For MSSPs, sediment samples are commonly taken from the surficial horizon (0 – 10 cm) and later analyzed at a certified laboratory to determine their chemical composition (Walker et al., 2013a). Given the low depth, surficial samples are typically collected with grab samplers. It is worth noting that this method has some limitations. This method only provides an overview of recently introduced chemicals, which is sufficient for ecotoxicity assessments. However, if these results are used for dredging purposes, grab samples may not cover historical contaminants found in deeper sediments. As dredging activities go deeper than the surficial horizon (> 50 cm), it is recommended to use other types of methodologies such as core samplers (Walker and Grant, 2009; Walker et al. 2013b).

Location of sample stations follows a random approach in accordance with the Environmental Protection Series: Users Guide to the Application Form for Ocean Disposal (Environment Canada, 1995 from AMEC). The study area is divided into a grid with five times the number of squares blocks as required stations. Specific blocks are then randomly selected to establish the sampling locations (Amec Foster Wheeler, 2015). Several factors can influence the number of stations. If there is stratification of sediment layers, lack of information on potential contamination sources, or nearby sensitive habitats, an increase of sampling locations can be justified (Walker et al., 2013a). If a MSSP has an adequate number of stations based on site-specific characteristics, contaminants variability and extremes can be decreased (Correll, 2007).

MSSPs used in this study were provided by Public Services and Procurement Canada (PSPC), the federal department which administers the program. Even though the 106 MSSP analyzed reports were carried out by different contractors, all of them reported the same parameters in sediment samples following the DFO and PSPC protocols. The complete list of MSSP parameters included: available metals, polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, benzene, toluene, ethylbenzene and xylenes (BTEX), polychlorinated piphenyls (PCBs), dichloro-diphenyl-trichloroethane, organaochlorine pesticides, total inorganic carbon, total organic carbon (TOC) and grain size. For this thesis, four classes of contaminants from the previous list were analyzed – PHCs, PCBs, PAHs and metals.

## 2.3 Petroleum hydrocarbons (PHCs) in marine sediments

### *2.3.1 Sources*

PHCs include crude oils and their refined products, which means thousands of individual compounds with wide-ranging physical and chemical properties (ITRC, 2018). They can have biogenic origins, like hydrocarbon seeps in the marine environment. While natural seeps can contribute to oil inputs into oceans, the presence of PHCs in marine environments is largely derived from anthropogenic activities such as in-land runoff, offshore industrial activities and oil spills occurring during production and transportation of oil (GESAMP, 2007). A study conducted by Little et al. (2015) in Milford Haven Waterway, Wales reported that 5-15% of PHCs in sediments had biogenic sources, while 70-85% were attributed to oil-industry related contamination and weathered historic spills. In Nova Scotia, certain shorelines have been historically subjected to oil spills. Chedabucto Bay, close to one the SCH included in this research (i.e., Canso – SCH 1) experienced the sinking of tankers in the last 50 years, affecting 300 km of coastline and reaching other SCHs in this study (i.e., Glace Bay – SCH 2) (Vandermeulen and Buckley, 1985; Yang et al, 2018a).

Onshore building and infrastructure located around the SCH wharfs are frequently heated by fuel oil, while boats themselves are refuelled from fuel tanks located at the harbour wharfs. Atlantic Canada is heavily reliant on PHCs due fuel oil for domestic home

heating. The main importing regions for refined petroleum products (RPPs) in Canada are the Atlantic provinces, Ontario and Quebec (CER, 2020). In 2018, RPPs were the largest fuel type consumed in Atlantic Canada, having a consumption per capita higher than the national average of 19.1 barrels (3,038 litres) (Fig. 2.2; CER, 2020). It is estimated that 58% of Canada's contaminated sites involve PHCs (FCSI, 2021).

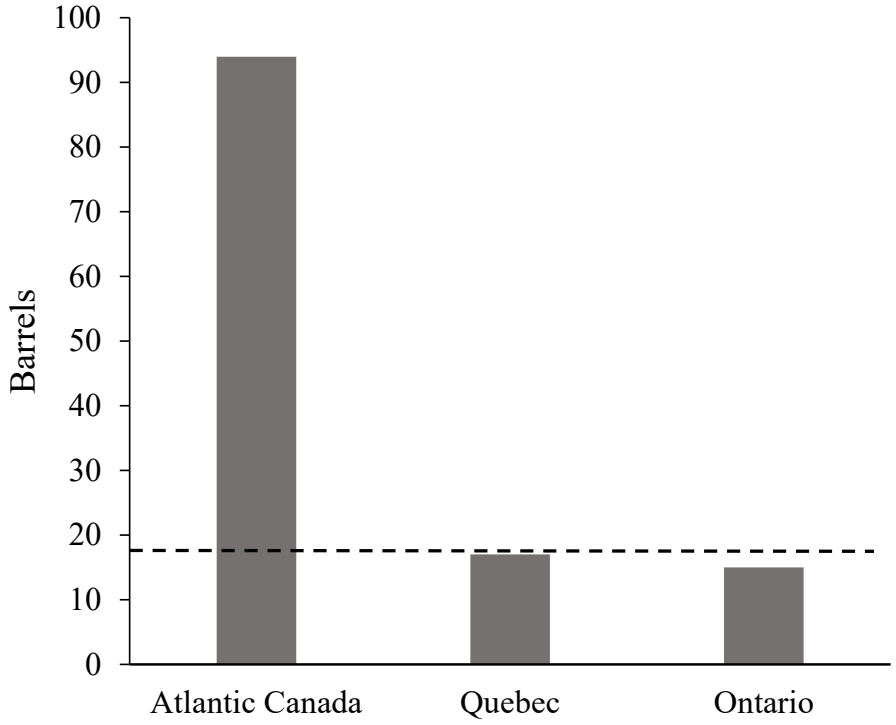


**Figure 2.2** RPPs consumption per capita in selected Canadian provinces. Horizontal dashed line represents national average of 19.1 barrels (CRE, 2020).

Major classes of PHCs are n-alkanes, branched alkanes, cyclo-alkanes, aromatics and alkenes (olefins). Crude oils and their derivatives are complex mixtures containing several of these compounds, covering a wide range of molecular structures and weights (Albers, 2003). However, these compounds can be categorized based on their density, volatility and viscosity, which is directly related to length of their molecular chains. The first category includes light oils and distillates that are highly volatile and thus evaporate quickly. They have a rapid dispersion and lower levels of toxicity given their short permanence on the contaminated site. Gasoline, petroleum ether and jet fuel are some examples of this classification. The second category includes products that are relatively

volatile and evaporate slowly, such as domestic fuels and diesel. The last group includes heavy oils that present very low volatility and long permanence in the environment (USEPA, 2017). A study carried out in the Bay of Fundy found that most samples sites along the shoreline had trace amounts of PHCs, but most sites had relatively low TPH concentrations. N-alkanes concentrations were mostly in the C16 to C35 range, with heavier PHCs (C29-C31) showing the highest values (Yang et al., 2018b).

### *2.3.2 Physicochemical and biological processes*

Once in the environment, PHCs go through a number of biophysical processes that can change their physical characteristics and chemical composition over time, known as weathering (Khan et al., 2018). Some of the main pathways for hydrocarbon weathering are volatilization, photodegradation, biotransformation, adsorption, and dissolution (Brassington et al., 2007). A contaminated site can have recently emitted hydrocarbons and/or weathered hydrocarbons as a result of long-term contamination. Molecular weight has an influence on the extent of hydrocarbon weathering, as heavier and more complex PHCs are normally the ones remaining after weathering, normally called an unresolved complex mixture (Frysinger et al., 2003). Weathering is an important consideration when assessing an impacted site since it can alter PHC behavior and distribution, as unresolved complex mixtures are more persistent and have a longer permanence in sediments (Reddy et al., 2002).

PHCs discharged into water bodies tend to spread quickly, forming sheens ranging from a few micrometers to several centimeters. Most PHCs have densities of less than 1 g/cm3, causing spills to initially float and remain on the surface (Connell, 2005). Heavy PHCs like crude oils and certain refined products begin to sink and migrate through the water column and into bottom sediments (NRC, 2003). Both crude oil and associated refined products suffer changes to their composition when exposed to sunlight, water, or air. Evaporation is more prevalent in light crudes and refined products like gasoline or low-molecular-weight fuel oils, it is estimated that crude oils can lose up to 45% of their volume through this physical process (Fingas, 2011). When PHCs are exposed to sunlight, a number of catalyzed reactions occur, which oxidize the carbons in PHCs. This

process is called photooxidation, where molecules in PHCs absorb sunlight and begin a number of photochemical reactions that degrade a wide range of products (D'Auria et al., 2008).

### *2.3.3 PHC interactions with organisms*

PHCs can adhere to different surfaces in the water column, such as plankton, sediment particles or detritus, precipitating into sediments for further degradation. Hydrocarbon-degrading communities play a key role in PHCs weathering in sediments, with over 900 distinct compounds being linked metabolically to aerobic degradation (Wardlaw et al., 2008). PHCs biodegradation is considered the main removal technique in soil, water and sediments (NRC, 2003). Microorganisms like bacteria, fungi and phytoplankton are mainly responsible for PHCs biodegradation in marine environments. Increase in molecular weight is directly related to PHC resistance to microbial degradation, both in water and soil (Varjani, 2017). Degradation of aliphatic hydrocarbons is faster than degradation of other compounds (Van Der Heul, 2011). N-alkanes are commonly the first hydrocarbons to be transformed by microorganisms in aerobic conditions. While limited under anaerobic environments, slow microbial biodegradation still occurs in these conditions.

Hydrocarbon partitioning in organisms is determined by the octanol-water partition coefficient of the compound ($K_{ow}$). This parameter is used to estimate the propensity of a compound to move from an aqueous phase into adipose tissue or body fat (Voutsas, 2007; Hermens et al., 2013). Hydrocarbon bioaccumulation can also be inversely related to the ability of an organisms to metabolize hydrocarbons through an enzyme called mixed-function oxidase (MFO). This enzyme converts lipid-soluble organic compounds into water-soluble metabolites, which are easier to eliminate from the body (Tugiyono, 2001; Cederbaum, 2015). High trophic level organisms like fish and certain crustaceans have well-developed MFO systems, allowing them to metabolize PHCs, only bioaccumulating when their habitats are heavily polluted (Uno et al., 2012; Koenig et al., 2012). MFO systems have also been reported in a number of aquatic invertebrates (Synder, 2000, Won et al., 2013; Han et al., 2014).

PHCs can have negative impacts on organisms due to habitat modification (decreased dissolved oxygen and food availability, changes in pH), physical action (reduced light, smothering, oiling) or toxicity (Albers, 2003). PHC toxicity will vary based on its composition and species affected. Benthic intertidal and shallow water communities are especially vulnerable following PHCs spills because of physical smothering, toxicity associated to absorption or ingestion, and/or oxygen depletion (Mendelssohn et al., 2012). Relatively immobile or sessile organisms like small invertebrates, plants and meiofaunal communities cannot escape and are severely affected. Intertidal presence of PHCs can also affect fish spawning (Quddus Khan et al., 2005). Short-lived species tend to recover faster. Bivalves can experience recovery periods of 5-10 years, while marine mammals may take decades to recover (Matkin et al., 2008).

Marine mammals are more vulnerable to oil exposure, since they have come up to the surface to breathe (Peterson et al., 2003). Light PHCs form a thin layer in the intertidal zone with potential to cause long-term impacts. Lighter fuels take to precipitate, which leads to more potential adverse effects on fish and other water-column organisms (Guerin, 2015). The most observed effects in fish are behavioral changes like decrease of swimming performance and impairment of respiratory functions. Long-term presence of these effects suggests that acute exposure to PHCs can have chronic impacts on fish populations (Johansen and Esbaugh, 2017). As fish deposit eggs and spawn close to the seafloor, impacts to fish embryos, particularly heart failure, may also occur as a chronic exposure effect (Incardona et al., 2009). Although aquatic organisms are commonly affected by oil discharges in the water, marine birds also suffer impacts from PHC contamination. The main effects are changes in their plumage microstructures, used for buoyancy and thermal insulation (O'Hara & Morandin, 2010). When oiled, bird feathers lose trapped air, leading to drowning or pneumonia due to lack of insulation. Birds experience an increase in their metabolic rate to compensate for loss of body heat and may also face starvation (Jenssen, 1994). Wiese and Robertson (2004) estimate that approximately 300,000 seabirds die each year as due to chronic oil pollution in waters surrounding Newfoundland and Labrador, Canada.

### *2.3.4 Environmental forensics and PHCs*

Environmental forensics is the investigation identification of the source and age of a pollutant through the application of specific analytical techniques (Morrison & Murphy, 2005). Since PHCs are a mixture of hundreds of different compounds, individual quantification on every contaminated site is unfeasible. When characterizing and assessing PHCs, tests for fractioned ranges of hydrocarbons are commonly used (ITRC, 2018; USEPA 2020). This classification measures the amount of PHCs in specific molecular weight ranges. One of the most notable methodologies was developed by total petroleum hydrocarbons (TPH) Criteria Working Group in the 1990s. This method divides PHCs into discrete fractions based on the length of their molecular chains. Additionally, physicochemical properties were determined for each fraction using the available data at the time. It has been widely accepted and adopted worldwide, including in Atlantic Canada (Chamberland et al., 2002). Based on their molecular ranges, the resemblance of product released into the environment can be broadly characterized. These reporting categories vary depending on the type of guideline or methodology used by analytical laboratories (Table 2.1).

**Table 2.1** Criteria for Canada-Wide Standards for Petroleum Hydrocarbons and Atlantic Risk Based Corrective Action, as well as the commonly reported fractions for analytical laboratories as a reference.

| **Guidelines** | **Criteria** | | | | |
|---|---|---|---|---|---|
| PHC CWS (CCME, 2008) | F1 C6 – C10 | F2 C10 – C16 | | F3 C16– C34 | F4 > C34 |
| Atlantic RBCA (Atlantic PIRI, 2012) | Modified TPH (Gas) | Modified TPH (Fuel) | | Modified TPH (Lube) | Not applicable |
| Analytical laboratories report for PHCs (Tier I) (Atlantic PIRI, 2016) | C6 – C10 | C10 – C16 | C16 – C21 | C21 – C32 | Not applicable |

## 2.4 Polychlorinated biphenyls (PCBs) in marine sediments

### *2.4.1 Sources*

Polychlorinated biphenyls (PCBs) are a category of synthetic organic compounds produced from 1929 to 1979 for different industrial and commercial uses (Fig. 2.2; NRC,

2001). Normally referred to by their trade names (e.g., Aroclor, Kanechlor, Clophen), PCBs consist of approximately 209 individual compounds or congeners (von Stackelberg, 2011). PCBs are classified as persistent organic pollutants (POPs) because of their resistance to biological and chemical degradation. The C – Cl bond is very uncommon in nature, so most enzymes are not capable of cleaving it (Erickson, 2020). Once released into the environment, these chemicals are very persistent given their chemical stability. They have bioaccumulative and biomagnifying characteristics, and may cause adverse effects in humans and wildlife (UNEP, 2013; Walker et al., 2013c).

Due to their chemical stability and physicochemical characteristics such as high boiling points, electrical insulating properties and lack of flammability, PCBs were widely used in heat transfer and electrical equipment, pigments, carbonless copy paper and dyes, and plasticizers in rubber, plastic and paint products, among other industrial applications (USEPA, 2021). It is estimated that the United States produced almost half of the PCBs globally between 1930 and 1977. France, Germany, and Russia each contributed to approximately 10% of the historical global production, with production last stopping in Russia in 1990 (Breivik et al., 2002). PCBs were released into the environment during their production, use, storage and disposal, as well as accidental spills and leaks. These releases continue to happen even after PCBs were banned in the United States in 1977 (Hopf et al., 2009). Urban areas are still known sources of PCBs releases into the atmosphere, particularly lower molecular weight congeners, presumably because of large reservoirs of PCBs in equipment and material still in use (Hornbucle and Robertson, 2010; Robson et al., 2010).While not manufactured in Canada, PCBs were still used in a variety of industrial activities for decades (Health Canada, 2021). There are multiple sources for PCBs in aquatic environments like SCHs, including land runoff, atmospheric deposition, leaching, and industrial wastewater discharge (Breivik et al., 2002; Davis et al., 2007).

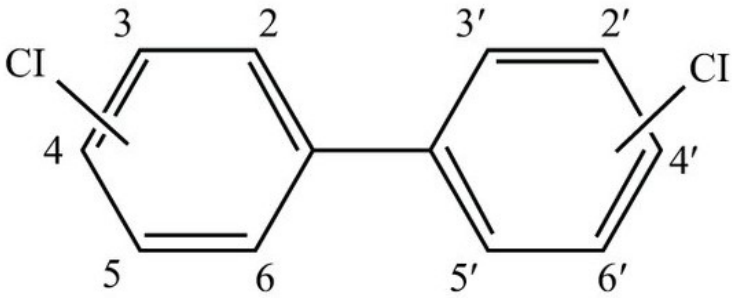


**Figure 2.3** General chemical structure of polychlorinated biphenyls (PCBs) (Faroon and Ruiz, 2016).

*2.4.2 Physicochemical and biological processes*

Classified as POPs, PCBs do not break down easily once released in the environment. They can cycle between water, air, soil and sediments for long periods of time (USEPA, 2021). PCBs are not soluble in water and have lipophilic properties, having an affinity for adipose tissue and sediments (Erickson, 2020). The hydrophobic characteristics of PCBs can be observed in their octanol-water coefficient ($K_{ow}$), a proxy used to estimate lipid/water partitioning from POPs. Total PCBs $K_{ow}$ values range between 3.90 and 8.23, making them up to $10^8$ times less soluble in water than in a nonorganic solvent like octanol (Jonsson and Carman, 2000; Linkov et al., 2005). PCBs rapidly adsorb to suspended particles in aquatic environments, precipitating and accumulating at different levels in the sediments. This affinity to sediments creates long-term reservoirs, which could act as potential secondary sources of contamination (Colombo et al., 2005).

PCBs are subject to weathering when exposed to the environment. The main physical weathering processes experienced by PCBs are evaporation and leaching. During chemical weathering (i.e., biodegradation and photochemical degradation), chlorine patterns are repositioned, or molecules are dechlorinated (Erickson, 2020). PCBs are not eliminated but the lighter congeners can be depleted first. While weathering does not transform one mixture or congener into another one, it can degrade them enough to resemble different products. These alterations are more noticeable when PCBs with higher fractions of low-chlorinated congeners are weathered (Johnson and Bock, 2014). A study of Aroclor 1242 weathering, an individual PCB used in paper manufacturing, found that as Aroclor 1242 profile started resembling heavier Aroclors as lighter

congeners were lost. The total PCB concentration also declined as samples experienced weathering (Saba and Boehm, 2011). Analysis of historically contaminated sediment cores suggests changes to PCBs due to physical and biochemical processes, as vertical distributions and concentration ratios of individual PCB congeners do not match commercial compositions (Santschi et al., 2001).

Sites that have been historically contaminated with PCBs have shown the development of communities capable of dechlorinating PCBs found in sediments (Bedard et al., 2005). Bacterial anaerobic dechlorination and aerobic oxidation are the main biodegradation pathways for PCBs in sediments (Passatore et al., 2014; Khalid et al., 2021). PCB-resistance and degradation capabilities have also been observed on some strains of native fungi from polluted sediments (Germain et al., 2021). Biological processes involving fungal strains endemic to a contaminated site have shown potential for mycoremediation (Sage et al., 2014). The metabolites and intermediate compounds found during ecotoxicological assays with ligninolytic fungi suggest the possible involvement of the monooxigenase system of cytochrome P450 in the degradation (Cvancarová et al., 2012).

### *2.4.3 PCBs interactions with organisms*

PCBs can adversely affect organisms because of their high Kow, as they accumulate in fatty tissue and can biomagnify in the food chain (Faroon and Ruiz, 2016). Biomagnification in the food chain has been modelled, among other approaches, using fugacity, a quantitative measure of the escaping tendency of a compound to partition from one phase to another (Johnson and Bock, 2014). It has been hypothesized that biomagnification occurs from a fugacity increase in the gastrointestinal tract as food is digested (Erickson, 2018a). PCBs effects can vary widely depending on the species and trophic level, with species in higher trophic levels in the aquatic food web being more impacted by biomagnification effects.

Benthic organisms such as burrowing invertebrates, crustaceans and bivalves are particularly vulnerable to PCBs given their binding to sediments (Tao et al., 2010; Walker et al., 2013c; Walker and MacAskill, 2014). While PCBs effects on fish depend

on their lipid content and trophic level, some of the pervasive consequences documented in fish include immunotoxicity, liver damage, behavioral effects, reproductive and thyroidal alterations (Fingerman and Russell, 1980; Fisher et al., 1994; Eisler et al., 1996; Walker and Peterson, 1994). Reproductive disorders such as premature pupping or infertility have been associated with PCB bioaccumulation in marine mammals. (Reijnders, 2003; Folland et al., 2016; Jepson et al., 2016). It can also be correlated with morphological and hormonal disorders in individuals (de March et al., 1998; Kannan et al., 2000; Genov et al., 2019). Seabirds can also experience reproductive disorders and birth defects. Behavioral changes have also been observed in individual impacted by PCBs contamination (Barron, et al., 1995; Guruge et al., 2001).

While commercial fishing does not happen in SCHs directly, there is potential for recreational fishing closer to the shore. For humans, exposure to PCBs through consumption of seafood is also possible if harvested species are caught where PCB levels are elevated (Domingo and Bocio, 2007). Shellfish filter large quantities of water as means to get their food, also bioaccumulating contaminants and sometimes serving as bioindicators of PCB contamination (Gueguen et al., 2011; Walker and MacAskill, 2014). Certain congeners have been associated to a higher risk on Hodgkin's lymphoma and prostate cancer, while maternal exposure to PCBs increased the risk of testicular cancer in their children (Hardell et al., 2004; De Roos et al., 2005; Ritchie et al., 2005). Consumption of PCB-contaminated fish has been also linked to endocrinal conditions in humas like decreased levels of thyroid hormones, especially in females (Persky et al. 2001). Regulatory agencies like the Canadian Food Inspection Agency have established thresholds to regulate chemical contaminants in fish products, with a limit of 2 mg/kg established for PCBs (CFIA, 2018; Walker et al, 2013c).

### *2.4.5 Environmental PCB forensics*

Environmental PCB forensics look to identify specific source commercial mixtures or by-products found at a particular site (Erickson, 2020). In certain places, it can be used to identify the parties potentially responsible for the presence of PCBs and impose liabilities to offset clean-up and remediation costs (USEPA, 2021). The number after the trade

name is normally associated with the percentage of chlorine by weight. If a compound has less chlorine atoms (e.g. Aroclor 1221 – 21% chlorine), it is going to be more volatile and soluble, as well as more biodegradable. More chlorine atoms reduce both volatility and solubility (USEPA, 2020). It is noteworthy that weathering in samples can skew identification of individual PCBs or deplete certain congeners when biodegradation has happened. As weathering can modify congeners profiles and ratios, samples could be misidentified when sent to commercial laboratories for analysis (Saba and Boehm, 2011; Erickson, 2018b). Analytical methods should be selected on a case-by-case basis to ensure the most adequate results are being obtained. Required detection limits, linier range, sensitivity and selectivity should be taking into account when selecting PCBs analysis techniques (Megson et al., 2016).

## 2.5 Polycyclic aromatic hydrocarbons (PAHs) and metals in marine sediments

PHCs and PCBs were the main focus of the characterization and overall research. A brief description of PAHs and metal effects on biota is also included in this thesis as they included in the multi contaminant ecological risk evaluation in Chapter 5. These two classes of contaminants have been extensively studied in the literature and were characterized in SCH sediments in Nova Scotia by previous researchers. For an in-depth and extensive description of PAHs and metals in the study area, refer to Davis et al., 2018; Davis et al., 2019a; Davis et al., 2019b; Zhang et al., 2019a and Zhang et al., 2019b.

### *2.5.1 PAHs*

PAHs are a class of lipophilic chemicals found ubiquitously in the environment. As PCBs, they present low water solubilities, having high sorption to particulate matter and affinity for sediments (Neff, 1979). It has been well documented that PAHs present carcinogenic, mutagenic and teratogenic effects in organisms due to their high toxicity (ATSDR, 2014). In Canada, most PAHs found in aquatic environments come from spills of petroleum products, metallurgical and coking plants, creosote-treated products and atmospheric deposition of incomplete combustion particles (ECCC, 2013). Sediments can act as deposition sinks for PAHs, accumulating over time. As PAHs in sediments may be

bioavailable for marine biota, they can cause acute and chronic effects if organisms are exposed to them (Neff, 2002; Reynaud and Deschaux, 2006). Benthic organisms with less developed metabolisms like polychaeta and bivalves may accumulate PAHs, but higher trophic biota are able to excrete them after a few days. However, they can still be impacted by acute and chronic toxicity when high amounts of PAHs are present (Neff, 2002; Neff et al., 2005; Van der Oost et al., 2003).

Sixteen individual PAHs have been designated as priority pollutants by the United States Environmental Protection Agency: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene, and dibenz[a,h]anthracene. They are considered to have a significant environmental concern because of their toxicity to organisms and persistence in the environment (Keith, 2014). While other individual PAH exist and can have effects in the environment, these 16 PAHs are the ones commonly tested and analyzed as part of environmental and human risk assessments (Zemo, 2009; Stout et al., 2015). These 16 individual PAHs have been previously analyzed in the study area. SQGs for the protection of aquatic life includes limit concentrations for individual PAH compounds and a class-specific one (total PAHs) (McGrath et al., 2019).

### *2.5.2 Metals*

While metals are elements that occur naturally in all ecosystems, anthropogenic activities can concentrate and redistribute metals to areas without natural sources, potentially causing adverse effects (USEPA, 2022b). Some examples of sources of metals in aquatic environments include discharges from mining activities, agriculture runoff, industrial effluents, urban sewage and landfill leachates (Gautam et al., 2016). In SCHs, potential sources of metals consist of leaching from debris in sediments (e.g., acid batteries), antifoulant paints and emissions from coal combustions and power plants. Once metals reach a body of water, then tend to precipitate and sorb to particulate matter or interact with inorganic compounds already present in sediments (Jamshidi and Bastami, 2016). Sediments are considered a secondary source of metal contamination, as disturbances can

allow for resuspension of metals, becoming bioavailable in the water column (Walker and MacAskill, 2014; Wang et al., 2015).

Even though certain metals are necessary for aquatic organisms, high concentrations of these compounds can disrupt their growth, metabolism or reproduction processes. Non-essential metals like lead, arsenic, cadmium, or mercury can have acute toxic effects even in trace amounts (Stankovic et al., 2014). Toxicity and bioavailability of metals in sediments can be influenced by a number of parameters, such as: metal binding phases in sediments (e.g., particulate organic carbon), that can reduce metal mobility, pore water chemistry (e.g., pH, redox potential, salinity) that also decrease metal availability, and sensitivity and behavior of benthic organisms, including historical exposures (Chapman et al., 1998). These factors should be taken into account when using metal SQGs to ensure screening levels have been correctly adjusted. SQGs for the protection of aquatic life have taken into account background concentrations of naturally occurring compounds like metals when developing screening levels, to distinguish natural versus anthropogenic origins of metals in sediments (CCME, 1995). Metal SQGs should also be appropriately compared to background concentrations on a site. If SQGs levels are lower than background values, an adequate alternative needs to be found, since aquatic organisms could have adapted to naturally elevated concentrations (Chapman et al., 1999). Nevertheless, SQGs have implemented appropriate analytical procedures to determine background concentrations at a site, such as using hydrofluoric acid to digest samples before analysis (CCME, 1995).

### 2.6 Sediment quality guidelines (SQGs)

To assess and determine potential ecological risk of any contaminant, its concentration must be compared to environmental quality standards. These guidelines provide concentration benchmarks that are used to interpret the data found for each site (Birch, 2018). Some factors that are considered when developing an environmental quality standard are media (i.e., air, soil, sediments, surface and groundwater), type of contaminant, type of land use and exposure pathways (Nova Scotia Environment, 2014). The approach in which these guidelines establish thresholds is based on concentration

values in which negative effects are likely to occur for biota. In Canada, Federal environmental quality guidelines are published by the Canadian Council of Ministers of the Environment (CCME). For this research, this SQG was used as a point of reference for individual PAHs, metals and total PCBs is the Canadian SQGs for the Protection of Aquatic Life (CCME, 2021). As there is no Federal framework for PHCs in marine sediment, this thesis used a regional SQGs for Atlantic Canada - Atlantic Risk-Based Corrective Action (Atlantic RBCA) (Atlantic PIRI, 2021). As MSSPs in SCHs are sometimes used to evaluate dredging disposal option, the *Canadian Environmental Protection Act* (CEPA) Disposal at Sea Guidelines (CEPA, 1999) was also used to evaluate total PCBs concentrations in SCH sediments.

### *2.6.1 Atlantic Risk Based Corrective Action (Atlantic RBCA)*

Atlantic RBCA is a tool used to assess and manage the remediation of sites impacted by PHCs in Atlantic Canada. It was developed by the Atlantic Partnership in Risk-Based Corrective Action Implementation (Atlantic PIRI) committee to provide both the environmental quality standards and a technical toolkit that environmental practitioners can use to carry out the risk assessment and remediation processes (Atlantic PIRI, 2012a). This tool follows a tiered approach to characterize and assess the risk in a potentially contaminated site. Atlantic RBCA combines TPH methodology with the ASTM Standard Guide for Risk-Based Corrective Action Applied at PHCs release sites to create a risk assessment tool specific to the characteristics and requirements of Atlantic Canada. Atlantic RBCA is also harmonized with the Canada-Wide Standards for Petroleum Hydrocarbons (PHC CWS) (Atlantic PIRI, 2012b).

As part of the Atlantic RBCA toolkit, there is software that facilitates evaluation and clean-up of impacted site. The software is an integrative modeling and risk characterization package that combines contaminant fate and transport models with an extensive chemical toxicity database to perform both Tier I (baseline risk screening levels) and Tier II/III (site-specific risk assessment) analysis (GSI Environmental, 2020). There have been four versions of the Atlantic RBCA guidelines since they were first published. Information presented in the screening levels section is taken from the latest

version, published in 2021. In 2006, Atlantic PIRI created an interdisciplinary group to revise and update accordingly the screening levels in Atlantic RBCA, to improve guidance and include ecological-focused criteria for sediments (Mroz et al., 2016).

For sediment screening levels, Atlantic RBCA used estimations from the PETROTOX model and the equilibrium partitioning framework (Atlantic PIRI, 2012b). The PETROTOX model was developed by Redman et al. (2012), being designed to simulate an aquatic toxicity test to predict acute and/or chronic effects on an organism caused by a certain concentration of PHCs (Redman et al., 2012; CONCAWE, 2020). For sediment, chronic and acute narcosis-based models were used to establish benchmarks, although other non narcosis effects were considered as well (Atlantic PIRI, 2012a).

The equilibrium partitioning model assumes that the toxicity of a chemical in sediments is the result of the chemical concentration in the aqueous phase. Partitioning behavior of an organic compound is a function of the chemical's organic carbon-water partitioning coefficient ($K_{oc}$) and the sediment's fraction organic carbon ($F_{oc}$) (Mroz et al., 2016). The quantification methodology is as follows: Sediment ESL = surface water ESL ($K_{oc}$)($F_{oc}$). This methodology allows for adjustments based on site-specific $F_{oc}$ (Tier I screening levels have a default $F_{oc}$ of 0.01), as long as it does not exceed 500 mg/kg TPH. Since PHCs concentrations tend to be reported under the PHC CWS fractions (F1-F4), one analytical consideration when using Atlantic RBCA ESL is to add F1-F3 data to calculate a single TPH concentration value (Mroz et al., 2016). To select appropriate TPH criteria, product type must be determined. This can be done through product resemblance (i.e., Atlantic RBCA criteria) or known site history. Depending on the resemblance, the sample is compared to the appropriate fraction concentration value (Atlantic PIRI, 2012b).

### *2.6.2 Canadian SQGs for the Protection of Aquatic Life*

The Canadian SQGs for the Protection of Aquatic Life provide concentrations references aimed to protect freshwater and marine aquatic life from adverse effects after periods of exposure to substances in sediments (CCME, 2022). These values are obtained from extensive evaluation of available toxicological studies documenting impacts to organisms

in different stages of their life from particular compounds (CCME, 1995). The guideline provides two thresholds, Interim SQGs and Probable Effect Levels (PELs). ISQGs are considered lower effect level concentrations, in which adverse effects are expected to rarely occur. On the other hand, PEL values are higher effect level concentrations, with effects expected to frequently occur (CCME, 2014-res). As these guidelines are used on a national scale, they were developed with a conservative approach. Exceedances of SQGs should be evaluated in conjunction with other site-specific information such as natural background concentrations or biological tests (CCME, 1995). Nevertheless, Canadian SQGs can surely be used as valid and consistent screening tools.

### *2.6.3 Disposal at Sea Guidelines*

The *Canadian Environmental Protection Act* (CEPA, 1999) regulates the disposal of approved substances at sea. Most of this material is dredged sediments moved to keep harbours clean and shipping channels operational (ECCC, 2005). A permit issued by Environment and Climate Change Canada (ECCC) must be obtained to dispose of dredged material, which requires sediments to be analyzed and be below screening levels for TPH, PAHs, metals, PCBs, DDT, and grain size (Walker et al., 2013a; ECCC, 2019). After completing disposal operations, sediments may need to be monitored annually to ensure compliance with permit conditions and that technical assumptions made during the approval process were valid and adequate to protect the marine environment (ECCC, 2015; ECCC, 2019).

## 2.7 Ecological risk

### *2.7.1 Ecological risk assessment*

An ecological risk assessment (ERA) is a process that assesses the probability of harmful ecological effects occurring in certain ecological components caused by the exposure to one or more contaminant (Jain et al., 2012). It evaluates if the presence of a substance exceeds hazardous levels, depending on the type of receptors and exposure pathway in the site. Evaluating the distribution and accumulation of pollutants is a vital step when carrying out ecological risk assessments, with the purpose of analyzing potential impacts of anthropogenic activities on marine ecological receptors (Walker et al., 2015b).

Following the assessment, management strategies can be used to decrease risks by eliminating the contamination source, reducing contaminant concentrations through remediation or applying administrative or engineering controls to reduce potential for exposure (Thalheimer & Parker, 2015). In Canada, there is a general framework form ERAs at Federal contaminated sites (FCSAP, 2012). ERAs in aquatic environments generally have a weight of evidence approach, where multiple lines of evidence are implemented to conduct the assessment (Walker et al., 2015b). Basic ERA framework encompasses the following fundamental stages (FCSAP, 2012; Stantec, 2017):

- Site characterization – A review of existing chemical and biophysical information, regulatory context and site management goals, as well as selection of potential contaminants of concern (CoC).
- Problem formulation – Nature and scope of the risk assessment, and analysis of gathered data to determine possible exposure pathways and potential ecological receptors. With this information, a conceptual site model (CSM) can be developed. CSM are graphical depictions of potential relationships between sources of CoC, exposure pathways and ecologic receptors (Fig. 2.4). CSMs can be seen as the bridging point between a baseline study and the following steps of conducting an ERA (Butt et al., 2020).
- Toxicity assessment – Selection of toxicity reference values and regulatory benchmarks for each potential CoC. These values will help determine protection goals and assessment endpoints. Lines of evidence for each endpoint are also developed at this stage.
- Exposure assessment – Types of exposures and total doses are estimated for each receptor in a specific pathway and for all potential CoC.
- Risk characterization – Quantitatively and qualitatively assessments of potential risk to receptors from exposure to potential CoC. This stage merges the results of the exposure assessment for each line of evidence and compares them to toxicity reference values. Findings will provide a concluding narrative that is clear and unambiguous regarding the level of risk.

- Uncertainty assessment – Uncertainties can occur throughout the ERA process (e.g., sample and analysis collection, derivation of toxicity reference values, professional judgements assumptions). Identifying and understanding these factors allows for the use of methods to provide accuracy and confidence ERA outcomes.

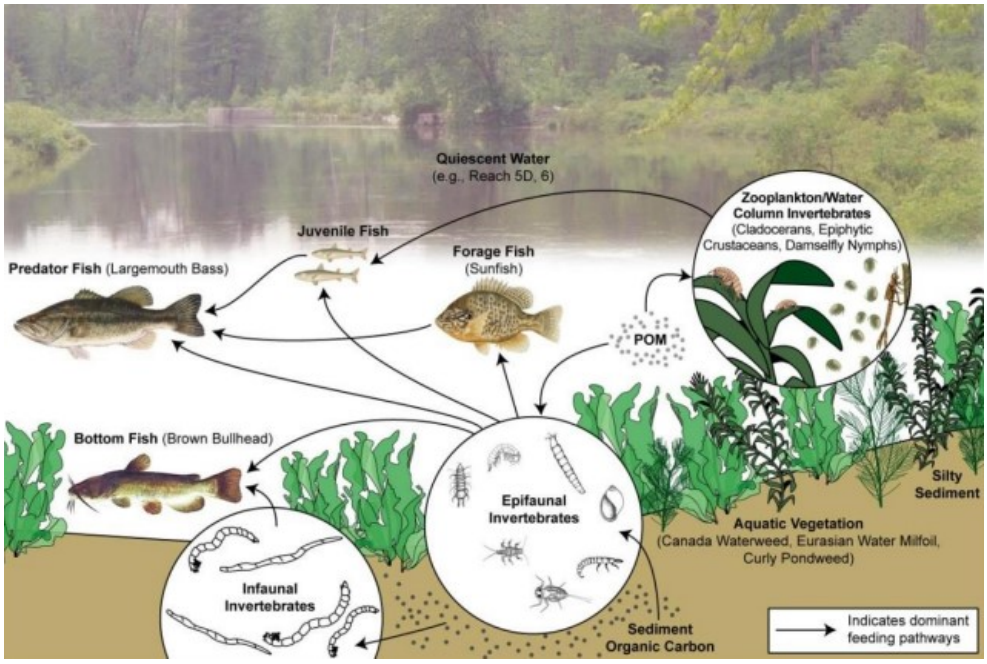


**Figure 2.4** Example of a pictorial conceptual site model displaying potential bioaccumulation pathways of sediment contaminants along the aquatic food chain (FCSAP, 2019).

Atlantic RBCA clean-up targets are also based on reducing risk to an acceptable level through any of these strategies (Atlantic PIRI, 2012b). This is closely related to historical and future land-use and activities at contaminated sites (Walker et al., 2015b). The risk methodology used in Atlantic RBCA for Tiers II and III (Atlantic PIRI, 2012b) follows a similar approach to a contaminated site as the ERA framework for Federal contaminated sites (FCSAP, 2012):

- Identify CoC and their respective concentrations at the site. Conduct site survey to identify receptors vulnerable to any hazards in the previous step.

- Carry out qualitative assessment of all potential exposure pathways, including but not limited to ingestion/dermal contact with soil/sediment, ingestion/dermal contact with groundwater, inhalation of hydrocarbon vapors.
- Carry out quantitative assessment of potential scenarios with highest risk of exposure.
- Estimate of receptors' chemical intake and resulting health effects.
- Calculate site-specific target levels.

As core SCHs are federally managed, risk-based strategies are useful to help harbour managers in the evaluation of the site's quality and potential contamination, as well as to determine any environmental liability present in the SCH. Understanding potential sources of contamination allows them to develop and implement adequate environmental management measures also relates to federal environmental liabilities and different environmental approaches (Zhang, 2019b). Risk assessments in SCHs provide a cost-effective way to approach remediation of contaminated sediments, allowing for prioritization of SCHs and providing scientifically defensible results to allocate resources (Kettlewell and Guest, 2014). The main objectives when managing contamination in SCHs is to identify and sample the sites that may be polluted, establish a liability and reducing that liability by remediation and risk managing activities the area (Meloche and McDonald, 2018). Public engagement after risk assessments is also an important component. As you can involve communities in certain clean-up and outreach activities, environmental awareness around SCHs can be achieved (McManus and Hamilton, 2019).

The Federal Contaminated Sites Action Plan (FCSAP) has also established a Framework of Addressing and Managing Aquatic Contaminated Sites (FCSAP, 2019). This framework provides ten steps to conduct extensive testing of a site and to develop and implement risk management strategies. Since this research is based on prior SCHs sampling programs and does not have a fieldwork component to it, it only covers the first four steps of the framework by identifying the aquatic site, carrying out a historical review, conducting an initial testing program and determining and initial site

classification. Thus, the portion of the study conducted in Chapter 4 will be referred to as an ecological risk evaluation of the study area rather than a full ERA.

### *2.7.2 Mean Probable Effect Level Quotient (mPEL-Q)*

Mean probable effect concentration quotients (mPEL-Q) measure the overall level of contamination in a sediment relative to a SQG, which is calculated by averaging the individual quotients for select parameters (MacDonald and Ingersoll, 2003). For this research, the SQG used in for this line of evidence is CCME PELs (CCME, 2021). Mean probable effect level quotient (PEL-Q) is a useful line of evidence since it combines multiple contaminants that could be found in sediments into a single value, while also providing likelihood of their toxicity (Long and MacDonald, 2006; Birch, 2018). It is calculated using the equation proposed by Long et al. (1995) (Eq. 2.1):

$$\text{mPEL-Q} = \Sigma\ (c_i/\text{PEL}_i)/n \qquad (2.1)$$

where $C_i$ is the concentration of each of the potential contaminants of concern (mg/kg), $\text{PEL}_i$ is the PEL for their respective threshold and n is the number of parameters being evaluated. Based on Long et al. (2000), mPEL-Q can be categorized into the following ranges: no risk (<0.1), low risk (0.11 – 1.5), moderate risk (1.51 – 2.3) and high risk (>2.3). It should be noted that, by getting a single value, the potential risk of individual classes of contaminants could be underestimated. mPEL-Q should be used along with other sediment quality approaches and lines of evidence to ensure that pollution levels are being correctly identified.

### *2.7.3 Frequency and number of exceedances*

The second line of evidence used in this study evaluated contaminant concentrations in SCHs that exceeded their applicable SQGs to assess possible effects to marine biota. To identify which compounds present the highest potential risk, it is necessary to determine the frequency and extent of SQG exceedances (Long and MacDonald, 1998). Frequency of exceedances considers the spatial distribution of potential effects, while the extent looks at the intensity of potential impacts (von der Ohe et al., 2011). Exceedances and their degree of difference from SQGs are calculated for each SCH and reported for each

parameter (Walker et al., 2015b). While some potential contaminant of concern may be extensively distributed, they may occur in rather low concentrations closer to their screening level. These analytes might be still of concern, but in terms of immediate actions, other compounds with higher extent may need to be prioritized (von der Ohe et al., 2011). This prioritization approach can help decision makers allocate resource and effort toward priority SCHs, as well as further risk assessment studies using other lines of evidence (Chapman and Mann, 1999).

# CHAPTER 3 SPATIOTEMPORAL CHARACTERIZATION OF PETROLEUM HYDROCARBONS AND POLYCHLORINATED BIPHENYLS IN SMALL CRAFT HARBOUR SEDIMENTS IN NOVA SCOTIA, CANADA*

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**Abstract:** Previous characterization of polycyclic aromatic hydrocarbons (PAHs) and metals has been conducted in small craft harbour (SCH) sediments in Nova Scotia, Canada, but petroleum hydrocarbons (PHCs) and polychlorinated biphenyls (PCBs) have not been spatiotemporally assessed. This study characterized the distribution of over 500 PHCs and PCBs samples in 31 SCHs sediments between 2000 and 2017. Federal and regional sediment quality guidelines were used to determine exceedances. Results showed exceedances for diesel and oil resembling PHCs, expected given their longer permanence in sediments and lower volatility. However, only 7% of the samples exceeded 500 ppm, threshold where benthic impairment and physical impacts from fouling are observed, showing low risk. PCBs do not pose high risk to biota since only six samples exceeded the higher effect level and 25% of them exceeded the lower effect one. Monitoring is recommended for SCHs with significant exceedances, as well as collectively assessing all contaminants characterized in SCHs.

**Key words:** Petroleum hydrocarbons (PHCs); Polychlorinated biphenyls (PCBs); Marine sediments; Sediment quality guidelines (SQGs); Small craft harbours (SCHs); Nova Scotia.

## Highlights

- Petroleum hydrocarbons (PHCs) and polychlorinated biphenyls (PCBs) were characterized in small craft harbour (SCH) sediments in Nova Scotia, Canada.
- Over 500 PHCs and PCBs samples in 31 SCH sediments were characterized between 2000 and 2017.
- Federal and regional sediment quality guidelines were used to determine exceedances.
- Exceedances were for diesel and oil resembling PHCs, but only 7% of samples exceeded 500 ppm threshold limits.
- PCBs do not pose high risk to biota (only 6 samples exceeded high effect and 25% of samples exceeded low effect levels).

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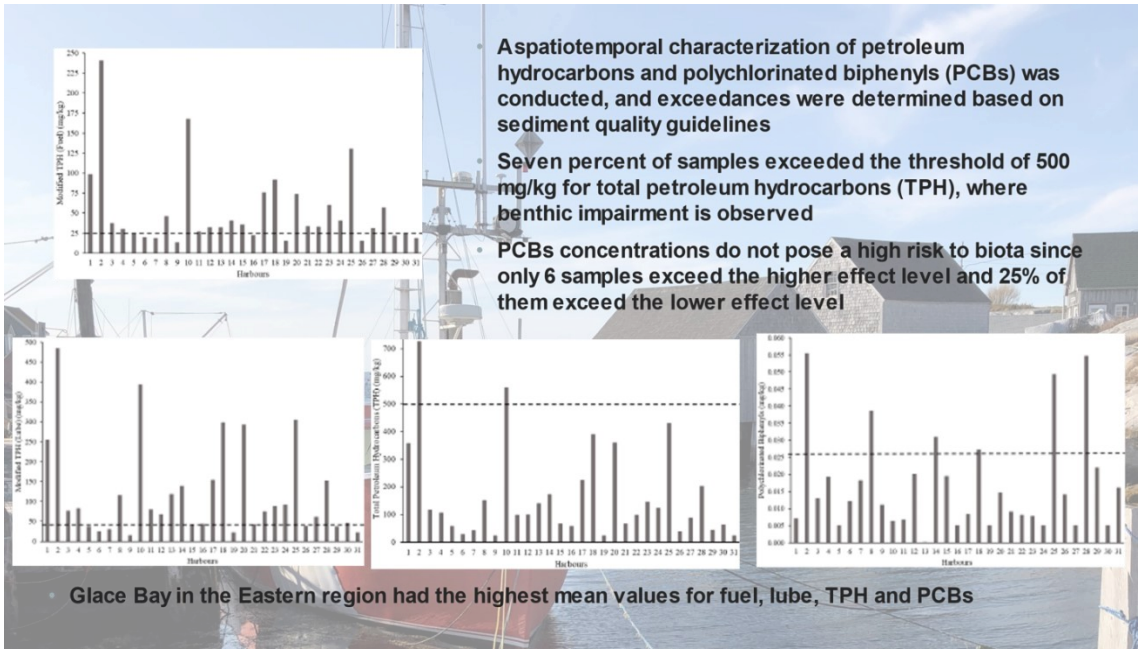
**Graphical abstract:**




## 3.1 Introduction

Small craft harbours (SCHs) in Nova Scotia, Canada are vital for the fishing industry, economy and have high socioeconomic and cultural importance for surrounding communities (DFO, 2019a). These harbours are managed nationwide through the Federal SCHs program run by Fisheries and Oceans Canada (DFO). Since September 2018, this program manages 1,008 harbours nationally, for fishing (87.5%) and recreational activities (12.5%). In total, these harbours have a value of approximately $5.6 billion CAD (DFO, 2019a). The main objective of the DFO SCHs program is to guarantee that fishing harbours are maintained in good conditions and operational. These harbours are classified as core and non-core. Core fishing harbours are defined as those crucial to the aquaculture and fishing industries, which are owned and managed by the DFO harbour authorities, while non-core harbours have been divested and are managed by third parties (Walker et al., 2015a; DFO, 2017). In 2016, the 178 fishing SCHs found in Nova Scotia accounted for 58.9% ($3.3 billion CAD) of the national infrastructure value for SCHs (Davis et al., 2018; DFO, 2016). In Nova Scotia, SCHs are divided into three management regions: Eastern Nova Scotia, Gulf Nova Scotia, and Southwest Nova Scotia (DFO, 2019b; Fig. 3.1).

The Eastern region covers the eastern part of Cape Breton, the eastern half of the south shore of Nova Scotia, and the Nova Scotia coast of the inner Bay of Fundy. The Gulf sector encompasses the Nova Scotia coast of the southern Gulf of St. Lawrence from the New Brunswick border to Bay St. Lawrence on the northern tip of Cape Breton. The Southwest region includes the southwestern half of Nova Scotia (DFO, 2019b). SCHs in the Digby Neck area, in Southwest Nova Scotia, area account for approximately $60 million CAD annually, providing hundreds of jobs to surrounding communities and are an important economic driver for the area (Standing Committee on Fisheries and Oceans, 2019).

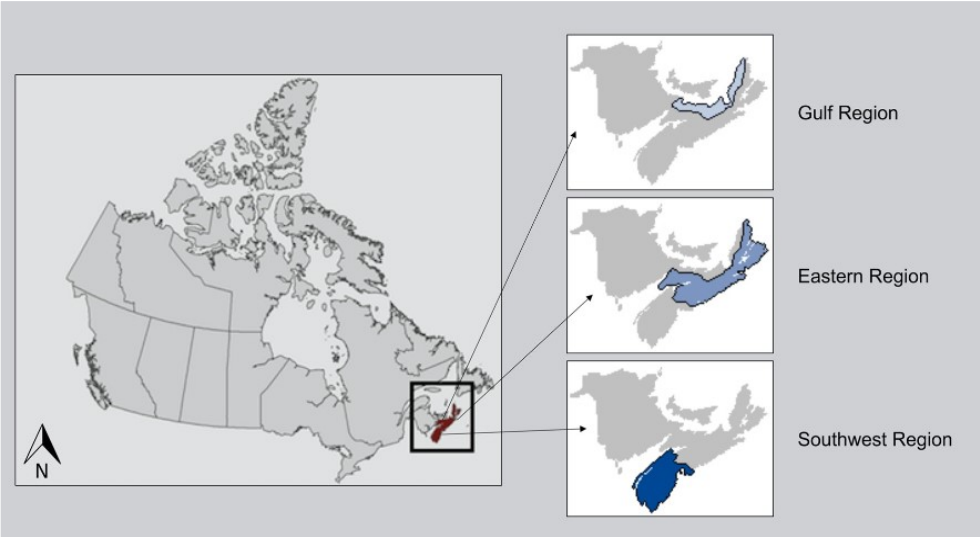



**Figure 3.1** DFO SCHs management regions in Nova Scotia (Davis et al., 2018).

Long-term fishing and recreational activities in SCHs have resulted in local sources of organic and inorganic contaminants which often impact harbour sediments (e.g., polycyclic aromatic hydrocarbons [PAHs] and metals) (Davis et al., 2018; Zhang et al., 2019a, Zhang et al., 2019b). Marine sediments are important because they provide habitat for a number of benthic epifaunal and infaunal species and influence the environmental fate of pollutants in marine ecosystems (Gray and Elliot, 2009). Numerous biogeochemical processes occur in marine sediments including sorption, sequestration, and degradation of organic matter (Nedwell et al.,1993; Nedwell and Walker, 1995;

Walker, 2005; Arndt et al., 2013). Near shore sediments with historical or ongoing anthropogenic activities, such as SCHs, can be subject to large influxes of contaminants, potentially affecting local aquatic ecosystems (Micheli et al., 2013; Walker and Grant, 2015). Several pollution sources can impact SCHs sediments, including petroleum hydrocarbons (PHCs) and polychlorinated biphenyls (PCBs).

PHCs are widely used compounds globally. In Canada, 106 billion litres of PHCs were used in 2019, with 81% being used for transportation fuel (NRCAN, 2021). However, such widespread use leads to some of these compounds being released into the environment, creating an increasing number of contaminated sites (Alboiu and Walker, 2019). An estimated 58% of contaminated sites in Canada involve PHCs (FCSI, 2021). These contaminated sites impact different media such as soil, surface water, groundwater, and sediments (Zafarani et al., 2022). PHCs include crude oils and their refined products, which can amount to thousands of individual compounds with wide-ranging physical and chemical properties (ITRC, 2018). PHCs can also have biogenic origins, like hydrocarbon seeps in the marine environment (Solomon et al., 2009). While natural seeps can contribute to oil inputs into oceans, the presence of PHCs in marine environments is largely derived from anthropogenic activities such as land runoff, offshore industrial activities and oil spills occurring during production and transportation of oil (GESAMP, 2007). A study conducted by Little et al. (2015) in Milford Haven Waterway, Wales, reported that 5-15% of PHCs in sediments had biogenic sources, while 70-85% were attributed to oil-industry related contamination and weathered historic spills.

Ecological impacts of PHCs in marine environments vary widely (NRC, 2003a; Lee et al., 2015). PHCs can have negative impacts on marine organisms due to habitat modification (decreased dissolved oxygen and food availability, changes in pH), physical action (reduced light, smothering, oiling) or toxicity (Alzahrani and Rajendran, 2019). Effects related to physical action and habitat modification are normally seen when significant amounts of PHCs are discharged (Albers, 2003). PHC toxicity will vary based on its composition and the species affected. Marine mammals are particularly vulnerable to oil exposure if there is a slick on the water surface, since they have to come up to the

water surface to breathe (Peterson et al., 2003). PHCs may cause various types of acute and chronic adverse effects on aquatic life (Guerin, 2015; Johansen and Esbaugh, 2017; Incardona et al., 2009; Quddus Khan et al., 2005).

Benthic intertidal and shallow water communities are especially vulnerable following PHC spills because of physical smothering, toxicity associated with absorption or ingestion, and/or oxygen depletion (Mendelssohn et al., 2012). Relatively immobile or sessile organisms, including various invertebrates, plants and meiofaunal communities cannot escape exposure and may be more severely affected. Short-lived species tend to recover faster from PHC spill events. For example, bivalves can experience recovery periods of 5-10 years, while marine mammals may take decades to recover (Matkin et al., 2008; Chang et al., 2014).

PCBs are a category of synthetic organic compounds produced from 1929 to 1979 for different industrial and commercial uses (NRC, 2001). Normally referred to by their commercial names (e.g., Aroclor, Kanechlor, Clophen), PCBs consist of approximately 209 individual compounds (von Stackelberg, 2011). Once released into the environment, these chemicals are highly persistent given their chemical stability (USEPA, 2020). They have bioaccumulative and biomagnifying characteristics, and may cause adverse effects humans in humans and wildlife (UNEP, 2013; Walker et al., 2013a). PCBs are subject to weathering in the environment. The main physical weathering processes experienced by PCBs are evaporation, photochemical degradation, biodegradation and aqueous leaching (Erickson, 2020). During biodegradation and photochemical degradation, chlorine patterns on PCB molecules are repositioned, or molecules are dechlorinated (Magar et al., 2005). Microbial degradation (biodegradation) of PCBs typically occurs at a very low rate due to the high toxicity of PCBs to microbial communities (Mousa et al., 1998). However, a number of aquatic sites with historical PCBs sediment contamination have shown the development of microbial communities that are capable of dechlorinating PCBs (Bedard et al., 2005). PBC-resistance and degradation capabilities have also been observed on some strains of native fungi from polluted sediments (Germain et al., 2021).

PCBs are lipophilic compounds that accumulate in fatty tissue causing neurological, endocrine, kidney and liver adverse effects in organisms (Faroon and Ruiz, 2016). For humans, exposure to PCBs through consumption of seafood is also possible if harvested species are caught where PCB levels are elevated (Domingo and Bocio, 2007). Regulatory agencies like the Canadian Food Inspection Agency have established thresholds to regulate chemical contaminants in fish products, with a limit of 2 mg/kg established for PCBs (CFIA, 2018).

Residual contamination can persist in marine sediments for decades, and may cause long-term impacts in sensitive coastal environments, including salt marshes (Culbertson et al., 2008; Reddy et al., 2002). Generally, long-term impacts of sediment contamination may result in reduced benthic invertebrate diversity and various indirect aquatic food web effects that may hinder ecosystem recovery (Zengel et al., 2015). Ecological impacts in marine sediments may also lead to effects in commercially harvested species and in human consumers of such species, potentially impacting fishing activities and local economy. For example, Sydney Harbour, Nova Scotia, has been historically impacted by PAHs and PCBs (Yeats, 2008), which has resulted in adverse effects in organisms like bivalves (Tay et al., 2003, Walker and MacAskill, 2014) and has also resulted in the closure of commercial lobster fisheries in the harbour since 1982, due to high levels of PAHs in lobster tissue (Hilderbrand, 1982, Walker et al., 2013c). Proper characterization, assessment and management of contaminated sediments in aquatic ecosystems are vital to avoid inappropriate aquatic site and adjacent land-use, inadequate cleanup activities and, primarily, impacts to human and ecosystem health (ITRC, 2018; Quanz et al., 2020).

The objectives of this study were to (1) identify the concentrations and distribution of PHCs and PCBs in SCH sediments across Nova Scotia and (2) compare PHC and PCB concentrations to Atlantic Risk-Based Corrective Action (Atlantic RBCA) and Canadian Council of the Ministers of the Environment (CCME) sediment quality guidelines (SQGs), and to *Canadian Environmental Protection Act* (CEPA) Disposal at Sea Guidelines, to determine the magnitude and frequency of guideline exceedances (CEPA, 1999; Atlantic PIRI, 2021; CCME, 2021).

## 3.2 Material and methods

### *3.2.1 SCH selection*

Previous studies have characterized PAHs and metal contaminants in SCH sediments in Nova Scotia (Davis et al., 2018; Davis et al., 2019a; Davis et al., 2019b; Zhang et al., 2019a, Zhang et al., 2019b), but none have comprehensively assessed PHCs and PCBs in SCH sediments. Harbour selection for prior studies were based on previous research by Walker et al. (2013b), which assessed cost-effective sediment dredge disposal options for priority SCHs in Nova Scotia. For research continuity and to compare to existing data, this study used the same 31 SCHs analyzed by Davis et al. (2018) and Zhang et al. (2019a). Six, nine and sixteen SCHs were selected from the Eastern, Gulf and Southwestern regions, respectively (Table 3.1; Fig. 3.2). All SCHs used in this research are core harbours, according to the DFO classification (DFO, 2019a). Coordinates for each SCH are included as supplementary material (Appendix A).

**Table 3.1** Selected SCHs classified by region and identified sequentially.

| Eastern Nova Scotia | Gulf Nova Scotia | Southwest Nova Scotia |
|---|---|---|
| 1. Canso | 7. Arisaig | 16. Battery Point |
| 2. Glace Bay | 8. Bailey Brook | 17. Centreville |
| 3. Neil's Harbour | 9. Barrios Beach Tracadie | 18. Clark's Harbour |
| 4. Owls Head | 10. Caribou Ferry | 19. Delap's Cove |
| 5. Port Morien | 11. Inverness | 20. Fox Point |
| 6. Three Fathom Harbour | 12. Judique Baxter's Cove | 21. Hampton |
| | 13. Pictou Landing | 22. Hunts Point |
| | 14. Pleasant Bay | 23. Little Harbour Shelburne |
| | 15. Skinners Cove | 24. Little River Yarmouth |
| | | 25. Moose Harbour |
| | | 26. Pinkney's Point |
| | | 27. Sandford |
| | | 28. South Side |
| | | 29. Stoney Island |
| | | 30. Westport |
| | | 31. Yarmouth Bar |

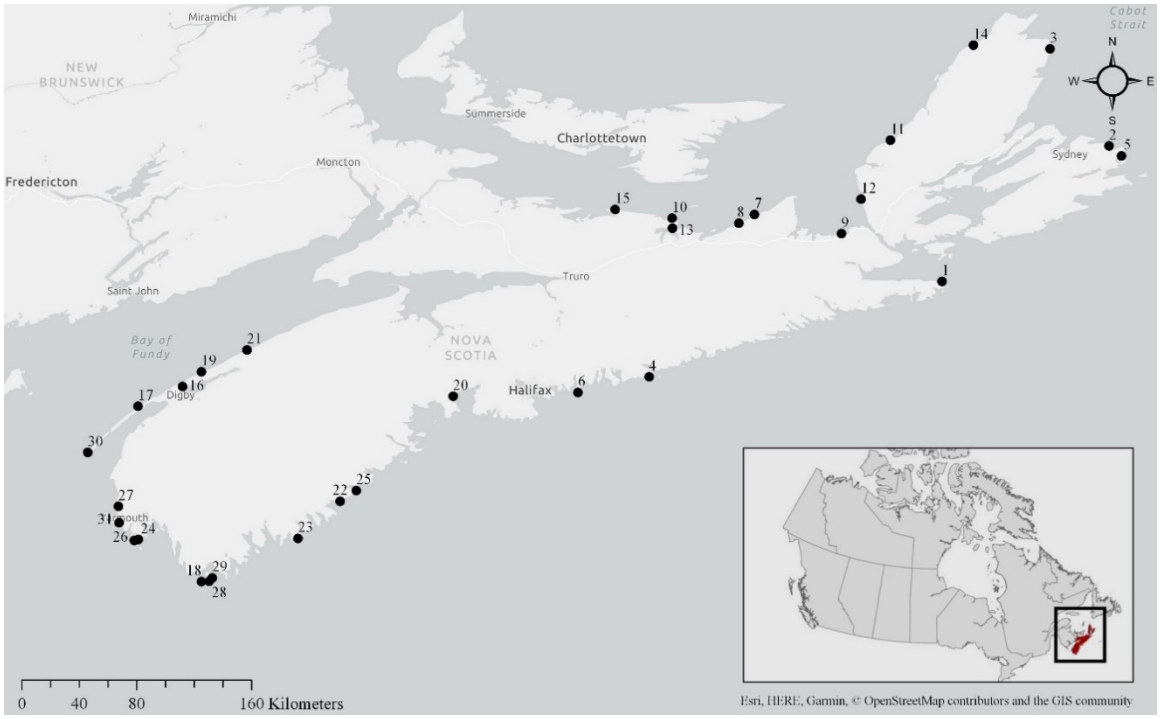



**Figure 3.2** Selected SCH locations in Nova Scotia [Inset map of Canada was produced by DMTI$^{TM}$].

### *3.2.2 Historical sediment data*

Sediment quality is monitored by DFO for each SCH individually through their Marine Sediment Sampling Program (MSSP) (Walker et al., 2013b, Davis et al., 2018). To conduct this study, historical SCH data was acquired from MSSP reports between 2000 and 2017. MSSP reports were supplied by Public Services and Procurement Canada (PSPC), the federal department which administers the program. MSSPs are used to characterize sediment quality of SCHs to compare results to applicable guidelines. MSSP studies help DFO characterize and delineate contaminated sediments prior to dredging operations for maintenance (to ensure navigable channels are maintained), for construction of new wharf of harbour structures, and to determine volumes of contaminated sediment for disposal (Walker et al., 2013b). A total of 528 sediment samples for PHCs and 531 samples for PCBs were used for this characterization (Table 3.2).

Sediment samples were collected from the surficial horizon (0-10 cm) from each sampling site (Walker et al., 2013b). While conducted by different contractors, all MSSP

reports analyzed identical parameters in sediment samples following the DFO SCH and PSPC protocols. The full suite of MSSP parameters included: available metals, PAHs, total petroleum hydrocarbons (TPH), benzene, toluene, ethylbenzene and xylenes (BTEX), PCBs, dichloro-diphenyl-trichloroethane, organaochlorine pesticides, total inorganic carbon, total organic carbon (TOC) and grain size (see Walker et al., 2013b).

**Table 3.2** Regional summary of number of reports and samples analyzed for each CoC.

| Region | Reports with PHCs Data (#) | Samples Analyzed for PHCs (#) | Reports with Total PCBs Data (#) | Samples Analyzed for Total PCBs (#) |
|---|---|---|---|---|
| Eastern | 14 | 72 | 18 | 88 |
| Gulf | 45 | 237 | 43 | 217 |
| Southwest | 47 | 219 | 50 | 226 |

The classifications used to characterize PHCs are the ones established in Atlantic RBCA (Atlantic PIRI, 2021): BTEX, modified TPH (Gas) (C6-C10), modified TPH (Fuel) (C10-C21), modified TPH (Lube) (C21-C32) and TPH. PCBs consist of 209 individual compounds (known as congeners), and PCB commercial products are normally referred to by their commercial names (von Stackelberg, 2011). MSSP reports provide the sum of all the individual PCB compounds, referred to as total PCBs. Total PCBs are the parameter analyzed in this study. These PHC and PCB parameters are the contaminants of concern (CoC) for the current study.

### *3.2.3 Sediment quality guidelines (SQGs)*

To assess and determine potential ecological risk of a specific contaminant, the contaminant concentration must often first be compared to environmental quality guidelines. These guidelines provide concentration benchmarks that are used to interpret data measured at each site (BC MOE, 2017). Some of the factors that are considered when developing an environmental quality standard are media (e.g., soil, air, groundwater, sediment), type of contaminant, type of land use and exposure pathways (Nova Scotia Environment, 2014). In Canada, SQGs include Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs), both of which were developed by the CCME for the protection of aquatic life in both marine and freshwater systems. CCME ISQGs are considered lower effect level concentrations and are associated with

concentrations where adverse effects are expected to rarely occur. On the other hand, CCME PELs are higher effect level concentrations. Effects may be expected to occur more frequently at these concentrations (CCME, 2021).

Canadian SQGs for total PCBs include CCME ISQGs and PELs (0.0215 and 0.189 mg/kg, respectively), as well as the CEPA Disposal at Sea Regulations guidelines (0.1 mg/kg) (CEPA, 1999). There are currently no national SQGs in Canada for PHCs. However, in recent years, Atlantic RBCA sediment ecological screening level for PHCs have been applied across Canada in many national contaminated aquatic site programs. These sediment screening levels were developed based on narcosis-based toxicity and equilibrium partitioning approaches (Atlantic PIRI, 2012). All screening levels are presented in Table 3.3.

### *3.2.4 Data and statistical analysis*

Descriptive statistics were calculated for the sediment concentrations of each CoC in every SCH that was evaluated, including measures of central tendency (mean, median), measures of variation (range, standard deviation) and frequency (counts, percent). An analysis of variance (ANOVA) was conducted to CoC concentration among SCHs, as well as Tukey's multiple pairwise comparison when applicable ($p<0.05$). To evaluate relationships between sediment CoC concentrations and physicochemical sediment characteristics, a Pearson correlation analysis was also carried out. All inferential analyses were completed using the IBM SPSS Statistics 26.0.0 software.

When sediment CoC concentration values were below reportable detection limits (RDLs), also known as "censored data", substitution methods were utilized. For PHCs, the censored data was replaced by the RDL itself. The research used this conservative approach since RDL and SQG concentrations are significantly apart (e.g., RDL for benzene is 0.003 mg/kg for most reports while the Atlantic RBCA screening level is 1.2 mg/kg). On the other hand, for PCBs, a ½ RDL was applied to censored data, as the RDL value is close in magnitude to the ISQG. The substitution of ½ RDL is commonly used as it depicts the potential central tendency of the undetected concentrations and it is a simple

methodology to utilize (Huybrechts et al., 2002; Singh and Nocerino, 2002). This replacement method is one of the recommended approaches for addressing non-detects by the United States Environmental Protection Agency (USEPA) (USEPA, 2000). In Canada, a study using various methods for estimating <RDL values from harbour sediments concluded that the use of ½ RDL showed similar mean values to other robust statistical methods (MacAskill, 2014). The ½ RDL method was also used by other studies that characterized contaminants in the selected SCHs (Davis et al., 2018, Zhang et al., 2019a).

### *3.2.5 Quality assurance and quality control*

All MSSP SCH sediment samples were processed by commercial laboratories with Standards Council of Canada (SCC), Canadian Association for Laboratory Accreditation (CALA) and/or SAI Global accreditation. Analytic procedures for specific CoC were based on recognized Provincial and USEPA methods. Every MSSP report includes laboratory QA/QC data were reviewed and all SCH sediment data were of adequate quality for assessment purposes.

## 4.3 Results and discussion

### *4.3.1 Mean sediment contaminant of concern (CoC) concentration comparison to SQGs and among small craft harbours (SCHs)*

A single mean sediment concentration was calculated for each CoC in all SCHs by combining all samples collected between 2000 to 2017. These values were compared to the applicable SQGs to identify any exceedances. None of the BTEX and modified TPH (Gas) fraction means calculated for each SCH exceeded guidelines (i.e., 1.2, 1.4, 1.2, 1.3 and 15 mg/kg, respectively). For the modified TPH (Fuel) fraction, 21 SCHs (67.74%) showed exceedances of the Atlantic RBCA screening level of 25 mg/kg. Across the evaluated SCHs, modified TPH (Fuel) fraction concentrations ranged from 13 to 240 mg/kg, with a mean of 51.7 mg/kg (Fig. 3.3a). Of the 21 SCHs, four are in the Eastern region, 7 in the Gulf region and 10 in the Southwest region (Fig. 3.4).

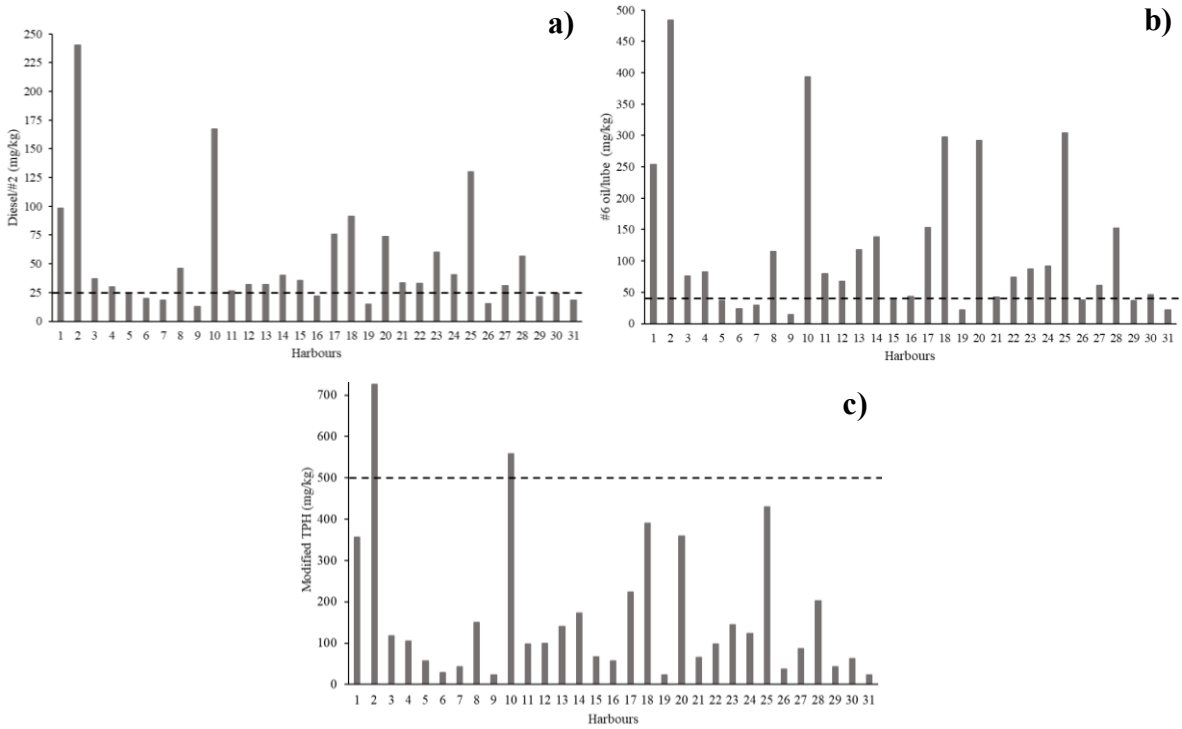



**Figure 3.3a-c** Mean concentrations in SCH sediments for modified TPH (Fuel) (a), modified TPH (Lube) (b) and TPH (c). Horizontal dashed lines represent Atlantic RBCA screening levels (25, 43 and 500 mg/kg, respectively).

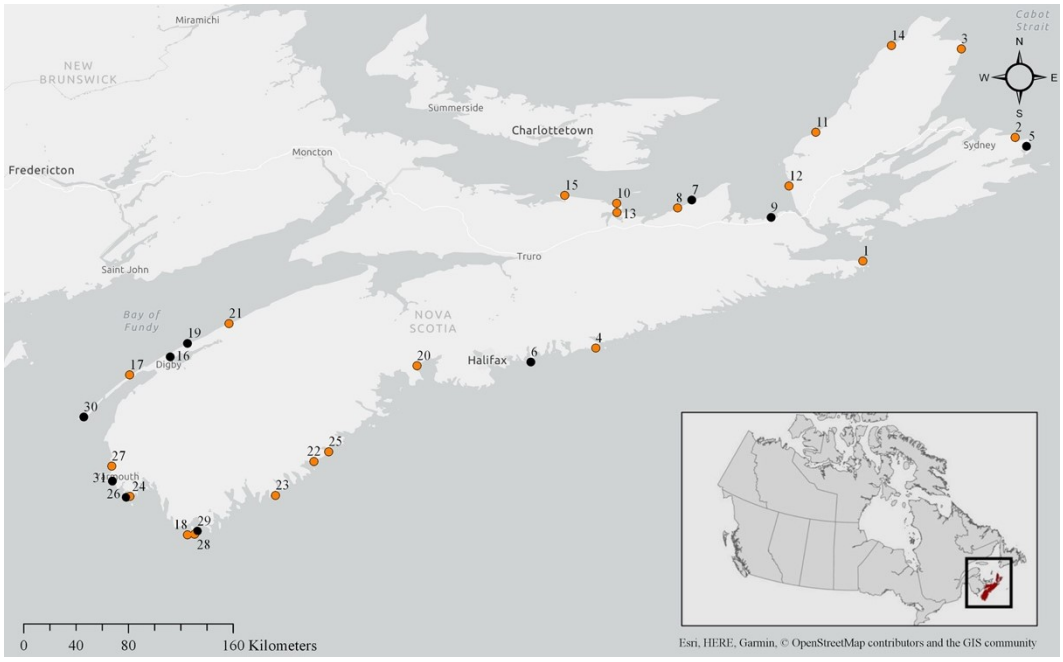



**Figure 3.4** Spatial distributions of modified TPH (Fuel) concentration exceedances across SCHs [Inset map of Canada was produced by DMTI$^{TM}$].

Similarly, 21 SCHs (67.7%) had sediment screening level exceedances for the modified TPH (Lube) fraction, where the screening level is 43 mg/kg. Concentrations of modified TPH (Lube) in SCH sediments ranged from 14.6 to 484 mg/kg, with a mean of 120 mg/kg (Fig. 3.3b). Of these 21 SCHs 4, 6 and 11 are located in the Eastern, Gulf and Southwest regions, respectively (Fig. 3.5). TPH represents the sum of all the hydrocarbon ranges. TPH concentrations in SCH sediments ranged from 22.9 to 726 mg/kg (mean 165 mg/kg) (Fig. 3.3c). There were only two exceedances (6.5%) for this parameter over the Atlantic RBCA screening level of 500 mg/kg; which occurred at Glace Bay in the Eastern region and Caribou Ferry in the Gulf region (Fig. 3.6). Overall, the Gulf region SCHs had the highest percentage of mean sediment PHC concentration exceedances for modified TPH (Fuel) fraction (33%), modified TPH (Lube) (28%) and TPH (50%).

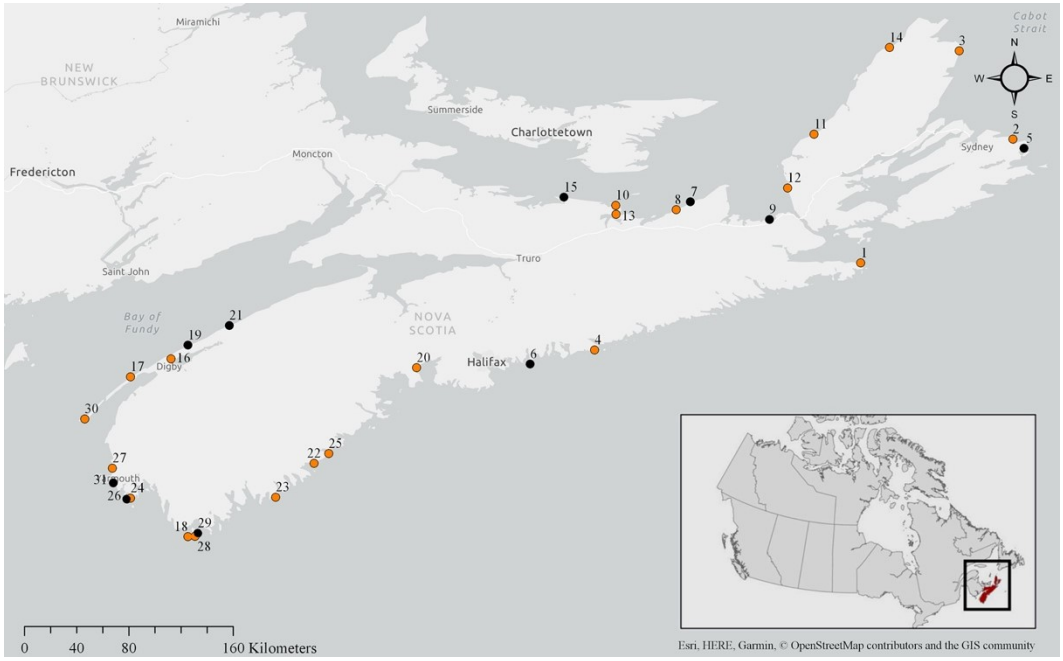



**Figure 3.5** Spatial distributions of modified TPH (Lube) concentration exceedances across SCHs [Inset map of Canada was produced by DMTI™].

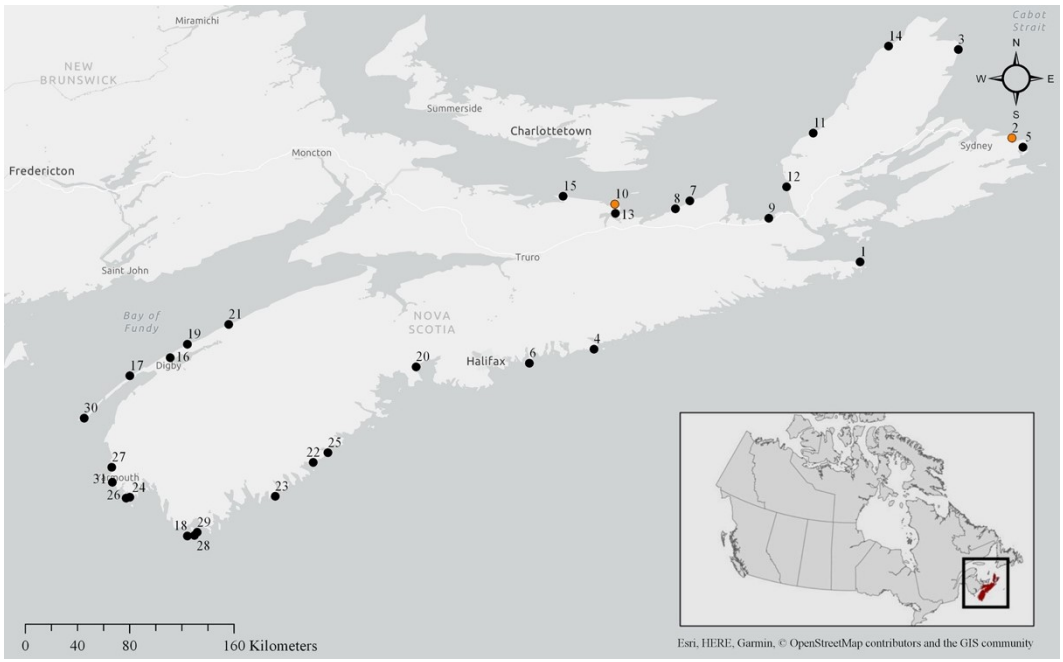



**Figure 3.6** Spatial distributions of TPH concentration exceedances across SCHs [Inset map of Canada was produced by DMTI$^{TM}$].

For total PCBs mean SCH sediment concentrations, there were no exceedances of CCME PELs (0.189 mg/kg) or CEPA Disposal at Sea Guidelines (0.1 mg/kg) at any of the assessed SCHs. Seven harbours had mean total PCB concentrations in sediment (25.8%) which showed exceedances over the CCME ISQG (0.0215 mg/kg). Total PCBs concentrations in SCH sediments ranged from 0.002 to 0.055 mg/kg (mean 0.017 mg/kg) (Fig. 3.7). The Southwest region SCHs had the highest percentage of ISQG exceedances with 57%. These SCHs were distributed as follows: 1 in the Eastern Region, 2 in the Gulf region and 4 in the Southwest region (Fig. 3.8).

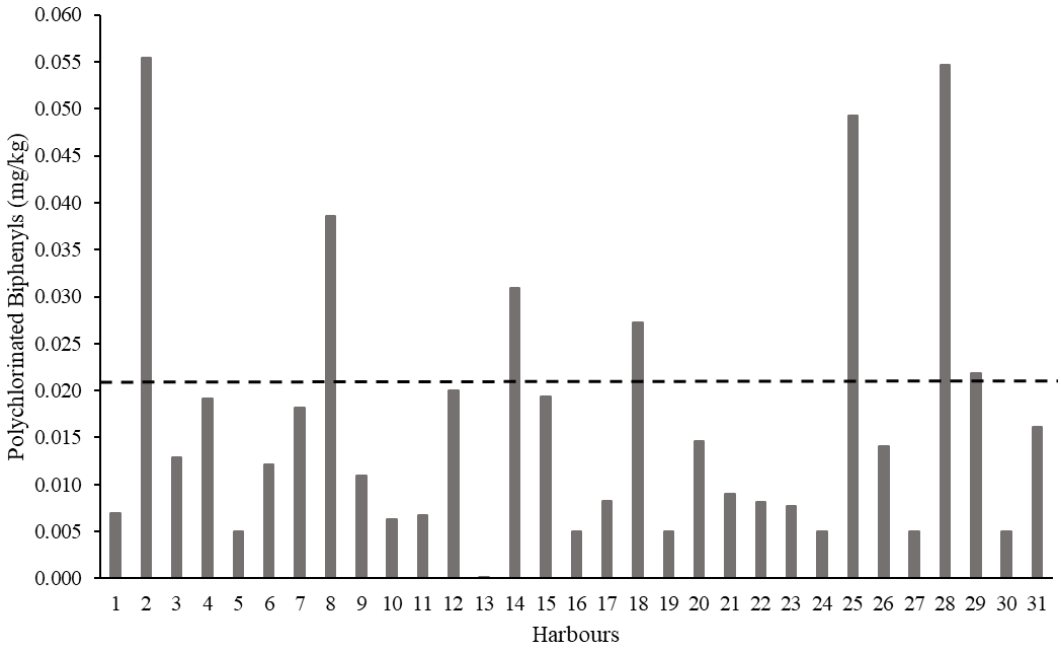



**Figure 3.7** Mean concentrations in SCH sediments for total PCBs. Horizontal dashed line represents CCME ISQGs (0.0215 mg/kg).

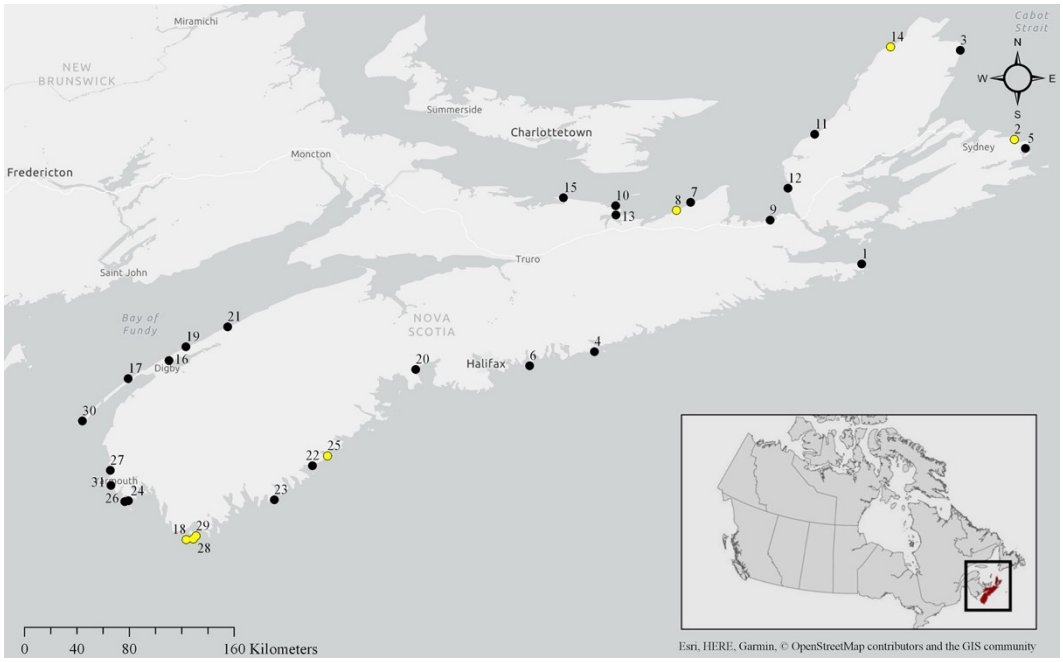



**Figure 3.8** Spatial distribution of total PCBs concentration exceedances across SCHs [Inset map of Canada was produced by DMTI™].

Of the total sediment samples assessed across all evaluated SCHs: one (0.19%) exceeded Atlantic RBCA screening levels for ethylbenzene; one (0.19%) exceeded Atlantic RBCA screening levels for xylene; two (0.38%) exceeded Atlantic RBCA screening levels for modified TPH (Gas); 200 (37.88%) exceeded Atlantic RBCA screening levels for modified TPH (Fuel); 262 (49.24%) exceeded Atlantic RBCA screening levels for modified TPH (Lube); and 37 (7%) exceeded Atlantic RBCA sediment screening levels for TPH. For total PCBs: 120 (22.6%) samples exceeded CCME ISQGs; 25 (4.7%) exceeded CEPA Disposal at Sea Guidelines; and six (1.13%) exceeded CCME PELs. The Eastern region presented the highest percentage of exceedances for the modified TPH (Fuel) fraction (51.38%), modified TPH (Lube) fraction (58.33%), TPH (16.66%), for total PCBs above CCME ISQGs, (34%) and for total PCBs above CCME PELs (2.2%).

Degree of difference is defined as how much an exceedance varies from the established threshold. A high degree of difference (indicates the CoC is present in large quantities on a site, but it may also be an indicator that the guideline is more conservative than expected (Davis et al., 2018). SQGs need to be continuously revised and updated, since they are based on empirical toxicity data, predictive models and criteria obtained from different jurisdictions. However, it should be noted that guidelines reflect the latest scientific knowledge available, and it must be assumed that they provide an appropriate benchmark to evaluate contamination on a site.

Ethylbenzene and xylene exceedances had very high degrees of difference (6.0 and 15.8 respectively). Since these two CoC have a very high volatility and both exceedances were single occurrences in this study, it is hypothesized that samples were affected after collection and do not represent the site conditions. Sediment screening levels used for modified TPH (Gas), modified TPH (Fuel) and modified TPH (Lube) are the default values established by Atlantic PIRI (2021). These screening levels can be adjusted to a higher concentration based on TOC values in a site, as long as they do not exceed 500 mg/kg. Since they are unadjusted to site-specific characteristics and use the most stringent values, it could indicate that screening levels used in this study can be deemed

conservative This is observed by modified TPH (Fuel) and modified TPH (Lube) having the highest means (Table 3.3). TPH has a mean degree of difference lower than two, indicating that most exceedances have concentrations close to the screening level. It is worth noting that the mean degree of difference for PHCs CoC are still low, suggesting that exceedances in SCH do not involve large quantities of PHCs. CCME ISQGs present a higher degree of conservatism than CCME PELs or CEPA Disposal at Sea Guidelines since they are based on lower effect levels (Table 3.4). For the higher effect level concentration (PEL), the mean degree of difference was below 1.5, showing that total PCBs sample concentrations are not present in large quantities in SCHs. A small degree of difference together with the low percentage of PEL and CEPA exceedances, the most stringent levels shows that PCBs are not an overall contaminant of concern in SCHs.

**Table 3.3** Atlantic RBCA screening levels exceedances and degree of difference for PHCs in Nova Scotia SCH sediments between 2000-2017.

| Contaminant of concern | Atlantic RBCA Screening Levels (Atlantic PIRI, 2021) | | |
|---|---|---|---|
| | Screening level (mg/kg) | # of exceedances (%) | Mean degree of difference (+/- SD) |
| Benzene | 1.2 | 0 (0) | 0 (N/A) |
| Toluene | 1.4 | 0 (0) | 0 (N/A) |
| Ethylbenzene | 1.2 | 1 (0.189) | 6.05 (N/A) |
| Xylene | 1.3 | 1 (0.189) | 15.8 (N/A) |
| modified TPH (Gas) | 15 | 2 (0.379) | 2.27 (0.93) |
| modified TPH (Fuel) | 25 | 200 (37.8) | 4.35 (5.57) |
| modified TPH (Lube) | 43 | 262 (49.2) | 4.88 (5.59) |
| TPH | 500 | 37 (7) | 1.98 (1.08) |

**Table 3.4** CCME Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Level (PELs) and CEPA Disposal at Sea Guidelines exceedances and degree of difference for PCBs in Nova Scotia SCH sediments between 2000-2017.

| | | | |
|---|---|---|---|
| CCME Marine SQGs (CCME, 2021) | ISQGs | SQG (mg/kg) | 0.0215 |
| | | # of exceedances (%) | 120 (22.6) |
| | | Mean Degree of Difference (+/- SD) | 2.92 (2.73) |
| | PELs | SQG (mg/kg) | 0.189 |
| | | # of exceedances (%) | 6 (1.13) |
| | | Mean Degree of Difference (+/- SD) | 1.35 (0.23) |
| CEPA (CEPA, 1999) | Disposal at Sea Guidelines | SQG (mg/kg) | 0.1 |
| | | # of exceedances (%) | 25 (4.7) |
| | | Mean Degree of Difference (+/- SD) | 1.59 (0.61) |

### *3.3.2 Distribution of CoC within SCHs*

Boxplot distributions are a helpful tool to visualize trends among CoC concentrations at each SCH. Figure 3.9a-c shows the distribution of selected CoC among individual SCH. Enhanced and enlarged versions of the three graphs are presented as supplementary materials (Appendix A). Outliers are noted with a circle, while extreme outliers (>3 interquartile range) are presented as asterisks. There is high variation in the distribution of the selected CoC across SCHs. Glace Bay (SCH #2) in the Eastern region appears to be the harbour most influenced by outliers and extreme outliers for all CoC. Distributions for modified TPH (Lube) resemble distributions for TPH. This is an indicator that PHCs present in the samples tend to have a resemblance to products and compounds in the lube oil range. Centreville, Clark's Harbour, Fox Point and Moose Harbour in the Southwest region exceed the screening level for TPH, indicating that this region may be more influenced by PHCs contamination. For total PCBs, only Moose Harbour (SCH #25) and South Side (SCH #28) in the Southwest region had exceedances of the CEPA Disposal at Sea Guidelines within the distribution (excluding outliers and extreme outliers). Across the rest of the SCHs, the exceedances for CEPA Disposal at Sea Guidelines and CCME PELs were outliers and extreme outliers (Fig. 3.10). SCHs had a different sample sizes because of the different number of MSSPs carried out on each of them. For some MSSPs, sampling stations were selected based on historic reports from a site (when available) and guidance from DFO, while other had a random selection implemented. Extreme concentrations could represent a potential concern, like a heavily contaminated area within a SCH. For total PCBs, outliers above CEPA Disposal at Sea Guidelines may suggest a potential problem, so further evaluation is recommended.

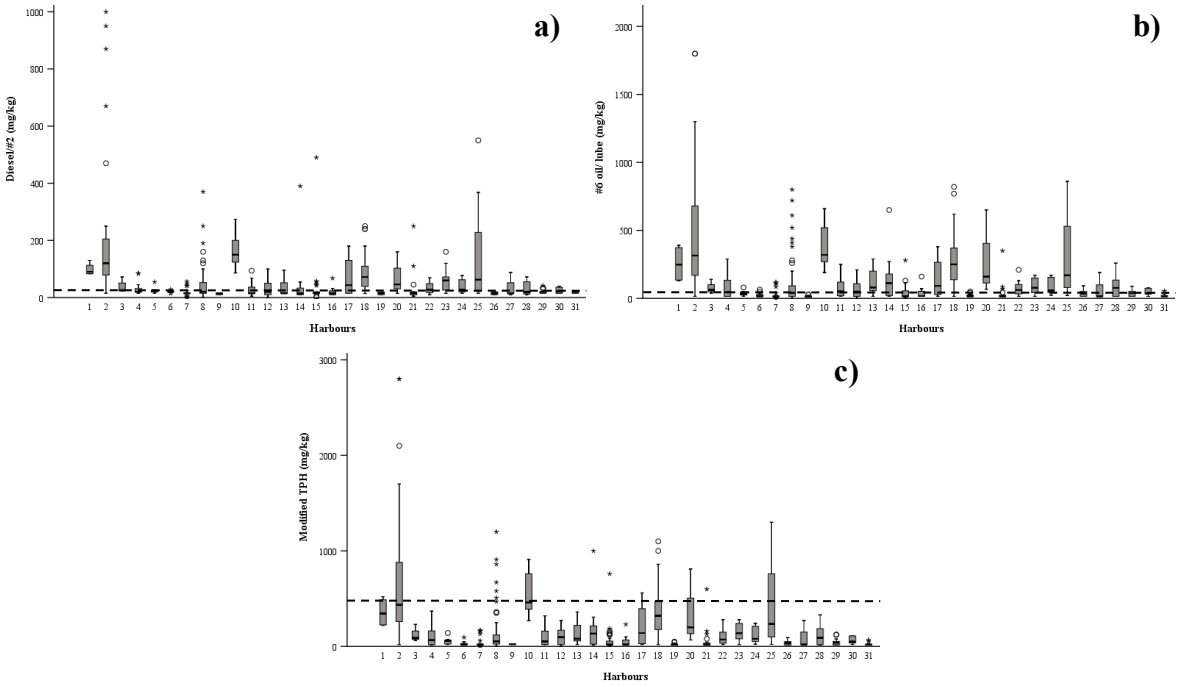



**Figure 3.9a-c** Distributions of modified TPH (Fuel) (a), modified TPH (Lube) (b) and TPH (c) concentrations across Nova Scotia SCHs. Horizontal dashed lines represents Atlantic RBCA screening levels (25, 43 and 500 mg/kg).

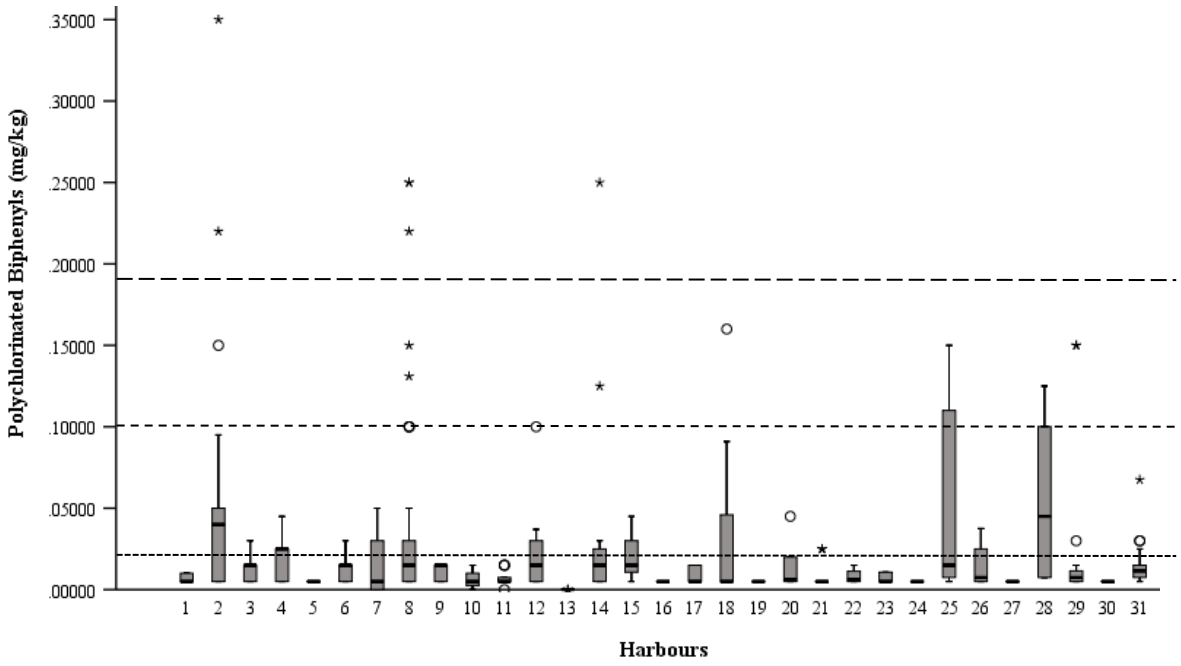



**Figure 3.10** Distribution of total PCBs concentrations across Nova Scotia SCHs. Various sediment quality guidelines (SQGs) are included as horizontal dashed lines. The smallest dashed line represents the CCME ISQG (0.0215 mg/kg), the medium dashed line represents the CEPA Disposal at Sea Guidelines (0.1 mg/kg) and the longest dashed line represents the CCME PEL (0.189 mg/kg).

### *3.3.3. Relationship with physical characteristics*

A Pearson correlation analysis was conducted between total PCBs and TPH. This characterization used values presented by Schober et al. (2018) to describe correlation strength, as follows: correlation coefficient <0.10, (negligible/very weak), between 0.10 and 0.39 (weak), between 0.40 and 0.69 (moderate), between 0.70 and 0.89 (strong) and >0.90 (very strong). The Eastern region showed a weak correlation (0.21), the Gulf region showed a negligible relationship (0.12), and the Southwest region had a moderate one (0.41). For all samples, correlation results were determined to be negligible (<0.15). PHCs and PCBs have different sources in SCHs, so the chances of there being any correlation are low.

Davis et al. (2018) collected and summarized physicochemical values from selected SCHs in Nova Scotia by determining mean values for each region. Results show that all three regions have a higher percentage of gravel and sand particles compared to finer particles like silt and clay. Mean TOC percentages across Nova Scotia SCHs were also characterized, with all regions being statistically similar to one another (Table 3.5). Particle size can influence the behavior and transport of CoC in marine sediments.

**Table 3. 5** Regional summary of SCH sediment physicochemical characteristics across Nova Scotia, reported as mean values with standard deviation in parentheses (Davis et al., 2018).

| Region | Gravel (%) | Sand (%) | Silt (%) | Clay (%) | TOC (%) |
|---|---|---|---|---|---|
| Eastern | 10.61 (14.72) | 49.32 (25.29) | 34.10 (23.21) | 11.31 (8.66) | 4.06 (7.78) |
| Gulf | 8.10 (15.14) | 49.99 (31.84) | 30.60 (23.95) | 14.39 (11.85) | 2.87 (12.53) |
| Southwest | 17.76 (22.10) | 54.39 (24.49) | 25.00 (20.52) | 9.69 (8.56) | 1.83 (2.16) |

*Note:* Values do not add up to 100% exactly, as percentages reported from commercial laboratories were reported as mean values for each region and these values were often truncated resulting in slightly higher values than 100%.

Nonpolar organic contaminants like PHCs and PCBs tend to partition best in fine-grained sediments like silt and clay (Reis et al., 2007). Organic matter also increases the affinity of these contaminants to sediments (NRC, 2003a). Generally, residual hydrocarbon saturation was inversely related to particle size (USEPA, 2004). A higher clay content and larger surface areas provide more binding sites for PCBs, limiting their bioavailability (CCME, 2001). Scholl (2000) found that high PHC concentrations are more persistent in lower permeability layers composed of clay and silt. Likewise, higher PCB

concentrations have been associated with finer grain sizes and high organic matter presence (Kampire et al., 2017). There tends to be less sorption and more contaminant degradation in higher permeability sediments like gravel or sand (Newell et al., 2013; USEPA, 2019).

A Pearson correlation analysis was conducted between the physicochemical parameter values (sand, clay and TOC) and CoC SCH concentrations. Correlation analysis results were consistent with previous research mentioned above, showing a negative correlation between CoC concentrations and sediment sand content. According to criteria from Schober et al. (2018), all CoC have a weak or negligible correlation with TOC (e.g., 0.1 to 0.39 or <0.1, respectively). There is a weak relationship between clay percentage and modified TPH (Fuel), modified TPH (Lube), TPH and total PCBs (0.33, 0.39, 0.38 and 0.11, respectively). The same CoC have a weak negative relationship with sand content (-0.28, -0.35, -0.33 and -0.12, respectively).

The Pearson correlation analysis was also conducted by management region to see if the overall results were consistent across Nova Scotia to see if CoC followed any potential trends across SCHs. In the Eastern region, lighter PHCs like BTEX and modified TPH (Gas) had a strong or very strong correlation with TOC, while heavier PHCs and total PCBs showed a weak or negligible relationship. All CoC had weak or negligible correlation with clay (+) and sand (-) except for modified TPH (Lube) and TPH, which presented a moderate inverse relationship with sand. For the Gulf region, there was no correlation between TOC and PHC CoC, only total PCBs showed a weak relationship. Modified TPH (Fuel), modified TPH (Lube) and TPH presented a moderate correlation with clay (+) and sand (-). For the Southwest region, modified TPH (Fuel), modified TPH (Lube), TPH and total PCBs had a moderate correlation with TOC. Modified TPH (Fuel), modified TPH (Lube) and TPH showed a moderate correlation with clay (+) and a weak one with sand (-). The rest of the CoC had a negligible correlation with the physicochemical parameters. Results were similar across management regions. The correlation between physicochemical parameters and CoC concentrations were stronger in management regions with more SCHs. However, the correlation analysis with all 31

SCHs for all relationships were weak or negligible. While it has been widely reported that physicochemical factors, such as TOC or grainsize, can influence contaminant partitioning and bioavailability (e.g., Walker et al., 2015b), this was not a strong confounding factor observed in SCHs for these specific contaminants (Zhang 2019a).

### *3.3.4 Mean CoC comparison to global harbours*

Mean concentrations and ranges of CoC in the 3 SCHs with highest values were compared to selected national and international harbours. Since TPH is the parameter most commonly used to report PHCs, only TPH was used for this comparison. Comparisons between the evaluated SCHs and global harbours were also made for total PCBs. It is worth noting that this comparison is only to contextualize results in this study, since each harbour has its own unique sources, reasons for sampling and sampling programs that were targeted. Sample location in these harbours in also relevant. However, we believe that this comparison provides a global view of CoC characterization. Data collected from more open channel samples can vary greatly from near shore water lots. Concentrations from SCHs and the selected global harbours were compared to the Atlantic RBCA screening level for TPH (500 mg/kg) to represent the PHC pollution level of each harbour (Table 3.6). For total PCBs, the harbour pollution level was represented by comparing mean concentrations to CCME ISQGs and CCME PELs (Table 3.7). Both CoCs have sediment concentrations that display wide variation across the three SCHs. TPH results in the SCHs showed similar trends to global harbours, where some harbours have exceedances but the mean value for each harbour rarely exceeds the Atlantic RBCA screening level.

**Table 3.6** Comparison of TPH in SCH sediments in Nova Scotia to selected global harbours.

| Location | TPH range (mg/kg) | TPH mean (mg/kg) | TPH Exceedances | Reference |
|---|---|---|---|---|
| Canada | | | | |
| Glace Bay SCH | 20-2800 | 725.63 | Yes | Present study |
| Caribou Ferry SCH | 270-910 | 558.89 | Yes | Present study |
| Moose Harbour SCH | 21-1300 | 439.61 | Yes | Present study |
| Halifax Harbour, NS | 32.5-8320 | 2141.25 | Yes | Jacques Whitford Environment Ltd. (1999) |
| Sydney Harbour, NS | 15-1300 | 311.6 | Yes | Walker et al. (2015b) |
| Saint John Harbour, NB | 10-30 | 20 | No | Yang et al. (2018) |
| Vancouver Harbour, BC | 2-260 | 20 | No | Yang et al. (2020) |

| Location | TPH range (mg/kg) | TPH mean (mg/kg) | TPH Exceedances | Reference |
|---|---|---|---|---|
| United States | | | | |
| Little Egg Harbor, NJ | 47-760 | 181.4 | Yes | Vane et al. (2008) |
| Mexico | | | | |
| Coatzacoalcos Harbour | 47.17-1290 | 475 | Yes | Albert et al. (2005) |
| Brazil | | | | |
| Todos os Santos Bay | 1.6-10.6 | 6.2 | No | Celino et al. (2008) |
| Uruguay | | | | |
| Montevideo Harbour | 451-3225 | 1837.6 | Yes | Muniz et al. (2015) |
| South Africa | | | | |
| East London Harbour | 12.59-1100 | 209.81 | Yes | Adeniji et al. (2017) |
| Taiwan | | | | |
| Kaohsiung Harbour | 1.9-22.6 | 4.33 | No | Lee et al. (2005) |
| Hong Kong | | | | |
| Victoria Harbour | 5.9-1996 | 284 | Yes | Zheng and Richardson (1999) |

**Table 3.7** Comparison of total PCBs in SCH sediments in Nova Scotia to global harbours. Total PCBs pollution level is estimated as low: <CCME ISQGs, moderate: >CCME ISQGs, <CCME PELs, high: >CCME PELs.

| Location | Total PCBs range (mg/kg) | Total PCBs mean (mg/kg) | Total PCBs Pollution Level | Reference |
|---|---|---|---|---|
| Canada | | | | |
| Glace Bay SCH | 0.005-0.350 | 0.055 | Low-High | Present study |
| South Side SCH | 0.008-0.125 | 0.055 | Low-Moderate | Present study |
| Moose Harbour SCH | 0.005-0.150 | 0.049 | Low-Moderate | Present study |
| Halifax Harbour, NS | 0.010-3.870 | 0.476 | Low-High | Jacques Whitford Environment Ltd. (1999) |
| Sydney Harbour, NS | 0.010-0.610 | 0.110 | Low-High | Walker et al. (2015b) |
| Saint John Harbour, NB | 0.003-0.018 | 0.008 | Low | Van Geest et al. (2015) |
| Vancouver Harbour, BC | 0.010-0.050 | --- | Low-Moderate | Bolton et al. (2004) |
| United States | | | | |
| Little Egg Harbor, NJ | 0.004-0.050 | 0.021 | Low-Moderate | Vane et al. (2008) |
| Boston Harbour, MA | 0.005-0.209 | 0.081 | Low-High | Massachusetts Department of Environmental Protection (2008) |
| Mexico | | | | |
| Mazatlán Harbour | --- | 0.017 | Low | Piazza et al. (2008) |
| Uruguay | | | | |
| Montevideo Harbour | 0.015-0.089 | 0.047 | Low-Moderate | Muniz et al. (2015) |

| Location | Total PCBs range (mg/kg) | Total PCBs mean (mg/kg) | Total PCBs Pollution Level | Reference |
|---|---|---|---|---|
| Norway<br>Oslo Harbour | 0.065-0.080 | 0.072 | Moderate | Cornelissen et al. (2008) |
| Italy<br>Naples Harbour | 0.001-0.899 | --- | Low-High | Sprovieri et al. (2007) |
| Hong Kong<br>Victoria Harbour | 0.001-0.097 | 0.018 | Low-Moderate | Richardson and Zheng (1999) |

TPH ranges and mean concentrations in Moose Harbour in the Southwest region compare favourably to values from the Coatzacoalcos harbour in Mexico. This harbour is intensively used by the oil and gas sector, with sources of contamination being studied in the past decades (Albert et al., 2005). Historical industrial effluents and accidental spills in the harbour and the river that flows into it have affected fisheries in the area, reducing the economic activity to mostly artisanal fishing (Bozada-Robles and Namihira-Santillán, 2005). The Coatzacoalcos is like SCHs in Nova Scotia since it supports small-scale fishing activities in the area, but it is larger and much more impacted by industrial activities than Nova Scotia SCHs, resulting in higher concentrations in sediments. Total PCBs range and mean concentrations in Glace Bay in the Eastern region are comparable to values from Boston Harbour in the United States. While Boston harbour has a legacy of historical contamination, remediation and improvement programs have been implemented in the past decades, which has resulted in downward trends for PCBs, among other pollutants (Hunt et al., 2006). These clean-up efforts may explain why this harbour has similar PCB values to smaller, less intensively used SCHs.

In the Canadian context, TPH and total PCBs concentrations from selected SCHs are generally lower than those in Halifax Harbour, Nova Scotia but higher than those in Vancouver Harbour, British Columbia. These two harbours are very different to SCHs since they are the largest ports in the eastern and western coast, and they have extensive commercial shipping activity (Levings et al., 2004; Robison et al., 2009). Halifax harbour has been historically subjected to several sources of contamination since the 18th century, causing heavy pollution in the area (Buckley et al., 1995). Higher concentrations of TPH

in Vancouver Harbour was close to densely urbanized areas and probably originated from historical oil spills and local industrial activities (Yang et al., 2020). SCHs do not tend to have legacy historical contamination like larger harbours. Communities around SCHs are also not highly developed like cities, where bigger harbours are located, which limits the amount of land runoff that can impact sediments. Additionally, large vessels that transit large harbours and ports are not used in SCHs, which generally support commercial fishing activities using smaller vessels (DFO, 2019). Furthermore, most SCHs do not have large and historical contaminant inputs from industrial activities like Sydney Harbour, which also showed higher concentrations for total PCBs, relative to Glace Bay, South Side and Moose Harbour.

### 3.4 Conclusion

Like previous studies of Nova Scotia SCHs, there was a significant variation in CoC distribution throughout SCH sediment, which could be attributed to dredging activities in certain SCHs that inhibit long-term buildup of CoCs in the sediments. While detailed information regarding dredging was not available, it is likely these activities could have a significant influence on the sediment data. This study showed that nearly half of the collected samples have exceedances for lube oil-resembling hydrocarbons across SCHs and 38% show exceedances of diesel-resembling hydrocarbons. Exceedances for these two PHCs categories were expected, because of their higher persistence in sediments and lower water solubility and volatility. A more prevalent concentration and distribution of modified TPH (Lube) indicated that presence of PHCs in SCHs mostly resembles heavier oil products with a bigger molecular size. Common activities in SCHs such as fuel use, transport and storage could also play a role as to why this PHC ranges were more frequent. However, only 7% of the samples exceed the TPH screening level (500 mg/kg). Interestingly, these exceedances are equally distributed across regions in Nova Scotia (12 in the Eastern Region, 12 in the Gulf region and 13 in the Southwest region). While sediment ecological risk assessments involving PHCs have not been conducted at the SCHs, these results suggest a low potential for ecological risk due to PHCs in sediments.

Given the distribution of total PCBs across SCHs, study results also suggest that total PCBs concentrations in SCH sediments likely do not pose an ecological risk to biota since they fall below CCME PELs and only 25% of SCHs had total PCB sediment concentrations that exceed CCME ISQGs, which is a more conservative guideline value. Bioavailability of persistent contaminants, including PCBs, is also influenced by their binding capacity to strongly sorb organic matter (i.e., black carbons like charcoal or soot) (Luthy et al., 1997; NRC, 2003b; Reichenberg and Mayer, 2006; Walker et al., 2013d). Laboratory aquarium experiments conducted by Fadaei et al. (2015) found that the presence of black carbon on sediments greatly reduces PCBs in exposure pathways and subsequent bioaccumulation in fish. Monitoring of sites that exceed CCME ISQGs for total PCBs and evaluation of data for other parameters like carbon is recommended to have a better holistic understanding of sediment contamination. Monitoring of SCHs that presented TPH exceedances is also recommended. While single contaminants may be below SQGs, interaction of multiple contaminants may potentially exacerbate ecological risk. Evaluating various contaminants already characterized in SCHs (i.e., PAHs and metals), in addition to PHCs and total PCBs is also recommended

# CHAPTER 4 MULTIPLE CONTAMINANT ECOLOGICAL RISK EVALUATION IN SMALL CRAFT HARBOUR SEDIMENTS IN NOVA SCOTIA, CANADA*

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**Abstract:** Small craft harbours are vital for the fishing industry and have high socioeconomic and cultural importance for surrounding communities. Presence of potential contaminants of concern in small craft harbour sediments can have significant impacts in biota and humans, including fishing activities and the local economy. While single contaminants sediment concentrations may be below sediment quality guidelines, the interaction of multiple contaminants in sediments may potentially exacerbate chemical ecological risk. An ecological risk evaluation for four classes of contaminants (i.e., petroleum hydrocarbons, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and metals) was conducted in 31 small craft harbours in Nova Scotia, Canada, using two approaches (i.e., mean probable effect level quotient and number and frequency of sediment quality guideline exceedances). Most small craft harbours showed a low ecological risk to marine biota, with only two small craft harbours suggesting high risk. While urgent action is not needed, monitoring is recommended for these small craft harbours to confirm that pollution is not increasing, and to potentially identify and control contamination sources.

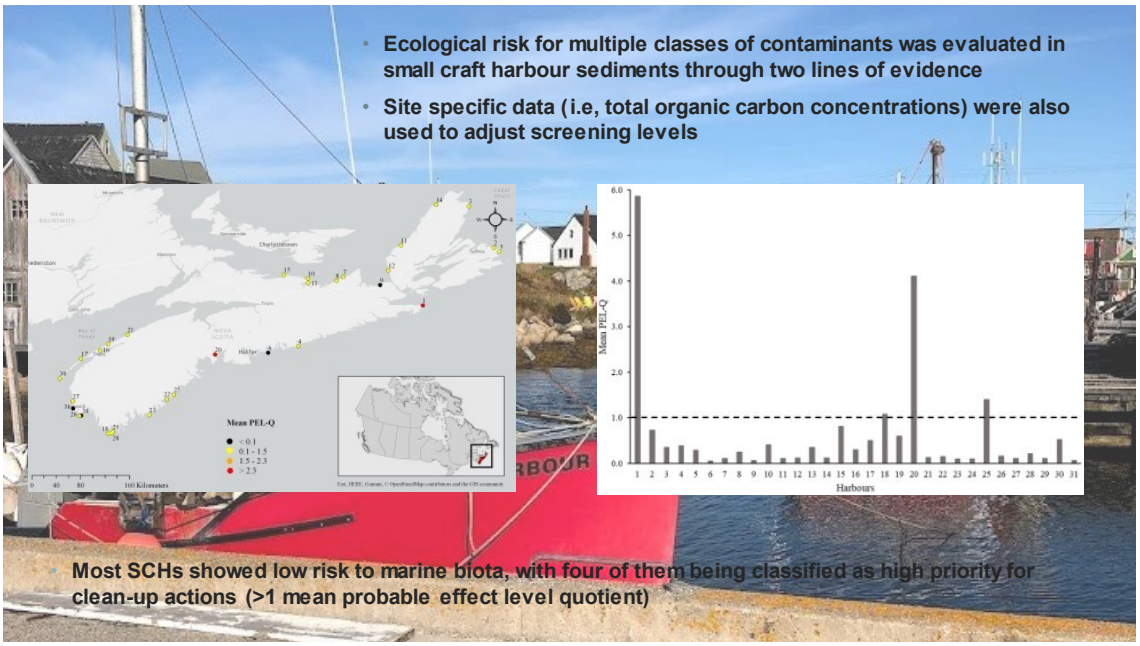
**Key words:** Ecological risk; Sediment quality guidelines (SQGs); Petroleum hydrocarbons (PHCs); Polychlorinated biphenyls (PCBs); Metal contaminants; Polycyclic aromatic hydrocarbons (PAHs).

## Highlights

- An ecological risk evaluation was conducted for small craft harbour (SCH) sediments in Nova Scotia, Canada.
- Four classes of contaminants were evaluated using two lines of evidence.
- Site-specific and sample-specific sediment organic carbon data were used to adjust sediment levels for PHCs.
- Of 31 SCHs evaluated, 4 were classified as “no risk”, 25 were classified as “low risk”, and 2 were classified as having “high risk” to marine biota.

** Prepared as an article for Science of the Total Environment, currently under journal review.*

## Graphical abstract




## 4.1 Introduction

Coastal areas provide important services that support livelihoods of surrounding communities, but they can be vulnerable to environmental changes, including climate change induced sea-level rise, and contamination (Lau et al., 2019). In Nova Scotia, Canada, fishing is an important economic activity, with a landed value of approximately $1.5 billion CAD in 2019 (DFO, 2021a; DFO, 2021b). Important coastal infrastructure to facilitate this activity are small craft harbours (SCHs). Fisheries and Oceans Canada (DFO) manages a program to maintain SCHs which are essential to the fishing industry, and to ensure that SCHs are in good working condition and operational (DFO, 2021c). SCHs in Nova Scotia are important socioeconomic drivers (Standing Committee on Fisheries and Oceans, 2019; Ragan, 2021). Nova Scotia has 178 SCHs classified into three management regions: Eastern Nova Scotia, Gulf Nova Scotia, and Southwest Nova Scotia (Fig. 4.1; DFO, 2021d).

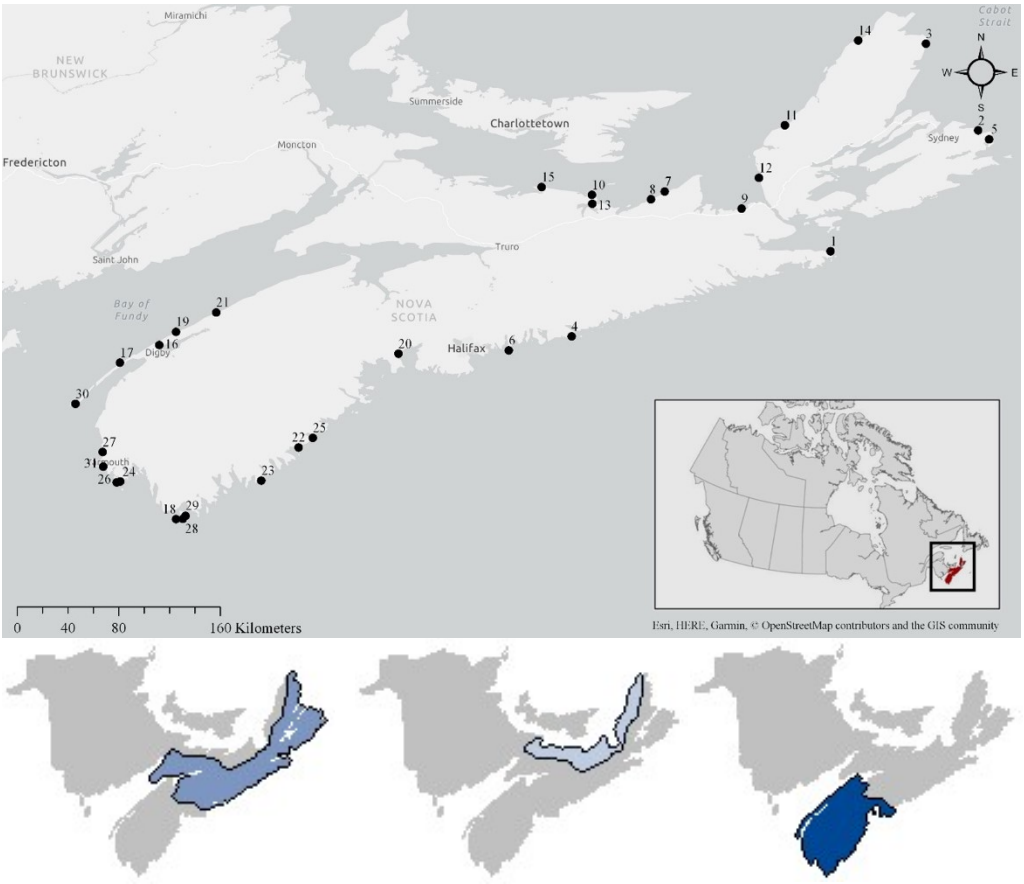



**Figure 4.1** Distribution of SCHs across Nova Scotia. SCHs are presented in the Eastern (n=6, bottom left), Gulf (n=9, bottom middle), and Southwest (n=16, bottom right) DFO SCH management regions in Nova Scotia. Adapted from DFO (2021d); Mora et al. (2022).

SCH sediments can be potentially contaminated as they are used for a wide variety of activities and may be located near inland contaminant sources like bulk fuel oil storage tanks (Kettlewell and Guest, 2014). When managing contamination in SCHs, the main objectives are to identify and sample sites that may be polluted, establish environmental liability, and reduce potential liability through remediation and/or risk management (Meloche and McDonald, 2018). Previous studies have characterized polycyclic aromatic hydrocarbons (PAHs), metals, petroleum hydrocarbons (PHCs) and polychlorinated biphenyls (PCBs) in SCH sediments in Nova Scotia (i.e., Davis et al., 2018; Zhang et al., 2019a; Mora et al., 2022). These studies were conducted on 31 SCHs across three management regions. Most contaminant sources in SCH sediments are related to boat repair and/or maintenance, as well as waste dumping in sub-tidal and inter-tidal areas (Meloche and McDonald, 2018). Zhang et al. (2019b) determined that given the wide

range of sources and types of contamination, a combined assessment of contaminant classes should be conducted to determine relative pollution levels and the potential for ecological risk. It is worth noting that, in this context, ecological risk from contaminants is solely focused on 'chemical-ecological risk', as risk to marine biota and ecosystems could come from multiple other sources.

Ecological risk evaluations or assessments can be used to provide an overview of the environmental state of SCHs and may facilitate prioritization of sites where further risk assessment and management may be required (Kettlewell and Guest, 2014). An ecological risk assessment estimates the probability of harmful ecological effects occurring in certain ecological components caused by exposure to one or more contaminants (Jain et al., 2012). Establishing the distribution and accumulation of pollutants is a vital step when carrying out risk evaluations that seek to assess potential impacts of anthropogenic activities on marine ecological receptors. A multiple lines of evidence approach is generally used in aquatic environments to assess ecological risk (Walker et al., 2015a; Quanz et al., 2020).

Meloche and McDonald (2018) developed a Conceptual Site Model (CSM) to assess and manage ecological risk in a SCH in British Columbia, Canada, which encompasses the main sources of contamination on the site (Fig. 4.2). Since most SCHs are federally managed by DFO, risk evaluations are also useful to ensure sustainable use and operation of SCHs and to determine any environmental liability present in the SCHs in case harbour divestment is being considered (Walker et al., 2015b).

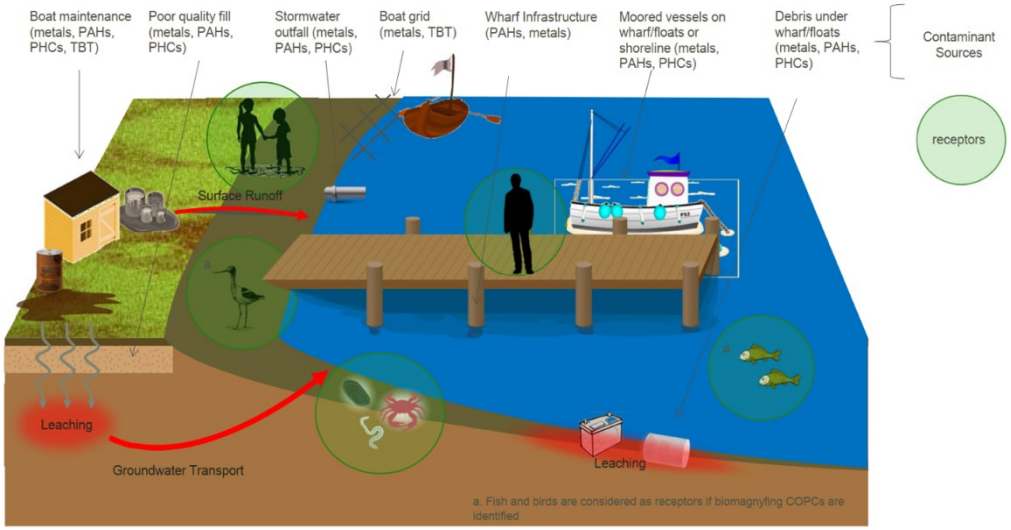



**Figure 4.2** Example of a conceptual site model for a small craft harbour (Meloche and McDonald, 2018).

The Federal Contaminated Sites Action Plan (FCSAP) has established a Framework of Addressing and Managing Aquatic Contaminated Sites in Canada (FCSAP, 2019). This framework provides 10 steps to conduct extensive testing of sites and to develop and implement risk management strategies. Since this study is based on previous SCH sampling programs and did not include a field sampling component, it covers the first four steps of the FCSAP framework by: identifying aquatic site(s), conducting an historical review, conducting an initial testing/assessment program, and determining an initial site classification. Thus, this study is referred to as an ecological risk evaluation rather than a full ecological risk assessment. The objectives of this study were to: (1) evaluate potential ecological risk posed by multiple contaminants in SCH sediments in Nova Scotia, and (2) determine the number and frequency of Canadian sediment quality guideline exceedances using site-specific SCH data.

## 4.2 Material and methods

### *4.2.1 Small craft harbour (SCH) and contaminant selection*

Harbour selection was made based on a previous study by Walker et al. (2013a) that assessed cost-effective sediment dredge disposal options for 31 priority SCHs in Nova Scotia. Six, nine and sixteen SCHs were selected from the Eastern, Gulf and

Southwestern regions, respectively (Table 4.1; Fig. 4.1). Previous research has been conducted in the same SCHs to characterize PAHs, metals, PHCs and PCBs (Davis et al., 2018; Davis et al., 2019a; Davis et al., 2019b; Zhang et al., 2019a; Mora et al., 2022). Historical SCH sediment data collected between 2000 and 2017 were used to characterize SCH contaminants from these previous studies. Data were acquired through the DFO Marine Sediment Sampling Program (MSSP) and Public Services and Procurement Canada (PSPC).

**Table 4.1** Selected SCHs classified by region and identified sequentially. Adapted from Mora et al. (2022).

| | | |
|---|---|---|
| Eastern Nova Scotia | 1. Canso | 2. Glace Bay |
| | 3. Neil's Harbour | 4. Owls Head |
| | 5. Port Morien | 6. Three Fathom Harbour |
| Gulf Nova Scotia | 7. Arisaig | 8. Bailey Brook |
| | 9. Barrios Beach Tracadie | 10. Caribou Ferry |
| | 11. Inverness | 12. Judique Baxter's Cove |
| | 13. Pictou Landing | 14. Pleasant Bay |
| | 15. Skinners Cove | |
| Southwest Nova Scotia | 16. Battery Point | 17. Centreville |
| | 18. Clark's Harbour | 19. Delap's Cove |
| | 20. Fox Point | 21. Hampton |
| | 22. Hunts Point | 23. Little Harbour Shelburne |
| | 24. Little River Yarmouth | 25. Moose Harbour |
| | 26. Pinkney's Point | 27. Sandford |
| | 28. South Side | 29. Stoney Island |
| | 30. Westport | 31. Yarmouth Bar |

Details about MSSPs in SCHs have been described in previous studies (Davis et al., 2018; Zhang et al., 2019a; Mora et al., 2022). MSSPs are used to determine the sediment quality of SCHs by comparing site sediment chemical concentrations to applicable sediment quality guidelines. Surficial sediment samples were collected from the 0-10 cm sediment horizon at each site (Walker et al., 2013a). The complete list of parameters included in MSSPs are metals, PAHs, total petroleum hydrocarbons (TPH), benzene, toluene, ethylbenzene and xylenes (BTEX), PCBs, dichloro-diphenyl-trichloroethane (DDT), total inorganic carbon (TIC), total organic carbon (TOC) and grain size (Walker et al., 2013a).

This study focused specifically on the risk evaluation of PAHs, metals, PHCs and PCBs. An ecological risk assessment for metals has been previously conducted in these SCHs (Zhang et al., 2019b). However, it is helpful to assess multiple contaminants together as they are normally found in combination at a site and this could influence the potential for ecological risk. Zhang et al. (2019b) determined that evaluating combined classes of pollutants could help harbour managers better understand the overall ecological risk of contaminants in SCH sediments.

Four contaminant classes were analyzed in this study (Table 4.2). Since BTEX concentrations were mostly below detection levels during the characterization process (Mora et al., 2022), they were not included for the ecological risk evaluation. Contaminant classes used for this study align with potential contaminants identified in the CSM by Meloche and McDonald (2018) in Fig. 4.2.

**Table 4.2** Contaminant classes and sample size.

| Parameter | Sample size (n) |
|---|---|
| PAHs[1] | 580 |
| Metals[2] | 576 |
| Total PCBs | 531 |
| PHCs[3] | 528 |

*[1]Thirteen individual PAHs: 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, naphthalene, phenanthrene and pyrene*
*[2]Eight individual metals: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn*
*[3]Four PHCs categories: modified TPH (Gas) (C6-C10), modified TPH (Fuel) (C10-C21), modified TPH (Lube) (C21-C32) and TPH (C6-C32)*

During previous assessments of SCHs, if sediment concentrations of PAHs, metals and PCBs were below detection levels (DLs), a ½ DL approach was implemented (Davis et al., 2018; Zhang et al., 2019a; Mora et al., 2022). Multiple approaches can be used when handling results below DLs. A ½ DL substitution approach can be unbiased for means if the analytical method used does not produce negative values, and if results between DL and zero are similar possibilities of occurring (Gilbert, 1987). The United States Environmental Protection Agency (USEPA) recommends substituting non-detects with ½ DL when the percentage of non-detects is below 15% (USEPA, 2000). MacAskill (2014) used a model for censoring data and found that even a complex model yielded the same

results as using ½ DL, and was used when analyzing PAH contaminants in sediments in Nova Scotia (MacAskill et al., 2016). For PHCs, the DL was taken as the concentration in situations where sediment samples had reported PHC concentrations below laboratory DLs. It is common practice to apply highly conservative approaches when assessing PHCs in sediments, since levels can be prone to analytical interference caused by biogenic hydrocarbons. All MSSP reports included Certificates of Analysis and quality assurance/quality control results by commercial laboratories that processed the samples. All laboratory quality assurance/quality control results indicated laboratory compliance with national and international standards, and all data were considered appropriate for assessment in this study. The two lines of evidence used for the ecological risk evaluation were i) mean probable effect level quotients (mPEL-Q), and ii) frequency and magnitude of exceedances over sediment quality guidelines (SQGs) for the assessed parameters.

### *4.2.2. Sediment quality guidelines (SQGs)*

SQGs are environmental benchmarks used by regulators and environmental practitioners to assess contamination levels of chemical contaminants in sediment (BC MOE, 2017). Several Canadian SQGs have been developed which consider the potential biological effects of chemical compounds (Burton, 2002; Quanz et al., 2020). Because SCHs are managed by DFO, federal SQGs are preferentially used for this evaluation. For individual PAHs, metals and total PCBs, the Canadian Council of Ministers of the Environment (CCME) has developed SQGs for the protection of aquatic life that include Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs) (CCME, 2021).

PHCs are not included in the current set of CCME SQGs. However, in Atlantic Canada, Atlantic Risk-Based Corrective Action (Atlantic RBCA) sediment ecological screening levels (ESLs) ESLs have been developed and have been widely used in SCH assessments since 2012. These ESLs were applied for comparison against sediment PHC concentrations.

The Atlantic RBCA ESLs are derived using the equilibrium partitioning method (Mount and DiToro, 2009). This method considers that the toxicity of a compound in sediments is

a function of its concentration in the aqueous phase (i.e., sediment porewater), its organic carbon-water partition coefficient, and the sediment fraction of organic carbon (Mroz et al., 2016). Non-polar organic compounds like PHCs tend to bind or sorb to sediment organic carbon, which may reduce their bioavailability to sediment organisms (Gobas and McLean, 2003; Thomann et al., 1992). Along with the equilibrium partitioning methodology, Atlantic RBCA ESLs are also based on the target lipid narcosis model (Atlantic PIRI, 2012).

The equilibrium partitioning basis of the sediment ESLs for PHCs allows for site-specific adjustments of the ESLs based on total organic carbon (TOC) concentrations in sediment samples. Briefly, the ESLs for PHCs can be multiplied by the TOC percentage in a sediment sample to yield a sample specific SQG, as long as it does not exceed the 500 mg/kg sediment ESL for TPH (Mroz et al., 2016; Atlantic PIRI, 2012). These adjustments are only allowable for the ESLs that were derived using the target lipid narcosis model and equilibrium partitioning approach. Such adjustments do not apply to the TPH screening level of 500 mg/kg, as this value was not derived on the basis of narcosis and equilibrium partitioning, but rather, is based on field studies of benthic community impairment from hydrocarbon spills (Atlantic PIRI, 2012).

For the modified TPH (Gas), modified TPH (Fuel) and modified TPH (Lube) parameters, each SCH sediment sample was evaluated in terms of its specific TOC value to determine if a sample-specific ESL could be developed. The Atlantic RBCA default TOC value of 1%, which is the assumption used in sediment ESL derivation, was assumed if sample-specific TOC was not reported or was <1% (Atlantic PIRI, 2012). The characterization conducted by Mora et al. (2022) used unadjusted Atlantic RBCA sediment ESLs, as it aimed to provide an initial analysis of PHCs in SCHs, without focusing on other site-specific sediment data. The current evaluation considers both unadjusted and TOC-adjusted sediment ESLs for modified TPH (Gas), modified TPH (Fuel) and modified TPH (Lube) in SCH sediment samples.

All SQGs used in this study have been regarded as highly protective and conservative values that are commonly used as indicators of potential sediment toxicity (Chen et al., 2013; Walker et al, 2015a; FCSAP, 2019). The SQGs for all parameters evaluated in this study are listed in Table 4.3.

### 4.2.3 Lines of evidence (LOEs)

The two lines of evidence (LOEs) used to evaluate potential risks to SCH sediment biota in this study were: i) mPEL-Q calculations, and ii) frequency and magnitude of SQG exceedances. In Nova Scotia, mPEL-Q and frequency of SQG exceedances have previously used as tools for assessing aquatic contaminated sites (e.g., Walker et al., 2015a; Zhang et al., 2019b).

**Table 4.3** Marine sediment quality guidelines (SQGs) for parameters in the SCH risk evaluation.

| Parameter | Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 2021) | |
|---|---|---|
| | ISQG (mg/kg) | PEL (mg/kg) |
| 2-Methylnaphthalene | 0.0202 | 0.201 |
| Acenaphthene | 0.00671 | 0.0889 |
| Acenaphthylene | 0.00587 | 0.128 |
| Anthracene | 0.0469 | 0.245 |
| Benzo(a)anthracene | 0.0748 | 0.693 |
| Benzo(a)pyrene | 0.0888 | 0.763 |
| Chrysene | 0.108 | 0.846 |
| Dibenz(a,h)anthracene | 0.00622 | 0.135 |
| Fluoranthene | 0.113 | 1.494 |
| Fluorene | 0.0212 | 0.144 |
| Naphthalene | 0.0346 | 0.391 |
| Phenanthrene | 0.0867 | 0.544 |
| Pyrene | 0.153 | 1.398 |
| Arsenic (As) | 7.24 | 41.6 |
| Cadmium (Cd) | 0.7 | 4.2 |
| Chromium (Cr) | 52.3 | 160 |
| Copper (Cu) | 18.7 | 108 |
| Mercury (Hg) | 0.13 | 0.7 |
| Nickel (Ni) * | 15.9 | 42.8 |
| Lead (Pb) | 30.2 | 112 |
| Zinc (Zn) | 124 | 271 |
| Total PCBs | 0.0215 | 0.189 |
| Parameter | Atlantic Risk-Based Corrective Action Ecological Screening Levels (mg/kg) (Atlantic PIRI, 2021) | |
| modified TPH (Gas) | 15 | |
| modified TPH (Fuel) | 25 | |

| | |
|---|---|
| modified TPH (Lube) | 43 |
| TPH | 500 |

*As CCME does not have ISQG or PEL values for Ni, effect range low (ERL) and effects range median (ERM) values from the US National Oceanic and Atmospheric Administration (NOAA) were used.

#### *4.2.3.1 LOE – Mean probable effect level quotient (mPEL-Q)*

mPEL-Q is a useful line of evidence since it combines the outcomes of SQG comparisons for multiple contaminants that could be found in sediments into a single value, and can also provide information on the likelihood for toxicity (Birch, 2018). It also offers a way to conduct normalized comparisons between different aquatic sites. MPEL-Q is calculated using the equation proposed by Long et al. (1995) (Eq. 4.1):

$$\text{mPEL-Q} = \Sigma\ (c_i/\text{PEL}_i)/n \qquad (4.1)$$

where $C_i$ is the concentration in sediment for each of the potential contaminants of concern (mg/kg), $PEL_i$ is the PEL SQG for each contaminant and $n$ is the number of parameters being evaluated. Based on Long et al. (2000), mPEL-Q can be categorized into the following ranges: no risk (<0.1), low risk (0.11–1.5), moderate risk (1.51–2.3) and high risk (>2.3).

In this study, 13 individual PAHs, 8 metals and total PCBs were evaluated using mPEL-Q, as PEL SQGs exist for these parameters. PHCs were not included in the mPEL-Q calculations. This is because the sediment screening levels for PHCs are not analogous to PELs, but rather, are calculated through the equilibrium partitioning method, as opposed to co-occurrence-based derivation methods, which serve as the basis for CCME PELs (Walker et al., 2015a; CCME, 2021).

#### *4.2.4.2 LOE 2 – Frequency, spatial pattern and magnitude of SQG exceedances*

Frequency, spatial pattern and magnitude of SQG exceedance per parameter and per SCH were also used as LOEs in this study. As each SCH had a different number of total sediment samples, relative frequency of SQG exceedance was expressed as a percentage as opposed to the number of samples in a given SCH exceeding SQGs.

In addition to frequency, the magnitude and spatial pattern of SQG exceedance was also evaluated. Degree of difference was used to determine exceedance magnitude and is defined as how much a substances' concentration in each sediment sample exceeds the established SQG (Davis et al., 2018; Mora et al., 2022).

Degree of difference is calculated by dividing a substances' concentration in a sediment sample by the SQGs for that substance. Spatial degree of exceedance was evaluated by visual examination of the SCH sediment samples with exceedances and preparing figures showing the locations of SCHs with SQG exceedances (Fig. 4.6-8).

## 4.3 Results and discussion

### *4.3.1 mPEL-Q*

As mPEL-Q is calculated on a per sample basis, Table 4.4 presents the mPEL-Q range and the average mPEL-Q determined for each SCH. Using the criteria from Long et al. (2000) and the average mPEL-Q for the assessed SCHs, 4 SCHs suggest no risk to benthic organisms, 25 SCHs suggest a low potential for risk, and 2 SCHs suggest a high potential for risk (Fig. 4.3).

**Table 4.4** Mean probable effect level quotient (mPEL-Q) range and average mPEL-Q across small craft harbour (SCH) sediment samples.

| SCH | mPEL-Q range in SCH sediment samples | Average mPEL-Q per SCH (+/- SD) |
|---|---|---|
| 1. Canso | 0.65 – 36.46 | 5.86 (10.14) |
| 2. Glace Bay | 0.09 – 5.65 | 0.73 (1.27) |
| 3. Neil's Harbour | 0.14 – 0.89 | 0.35 (0.23) |
| 4. Owls Head | 0.04 – 1.2 | 0.38 (0.35) |
| 5. Port Morien | 0.04 – 0.65 | 0.29 (0.17) |
| 6. Three Fathom Harbour | 0.01 – 0.12 | 0.05 (0.03) |
| 7. Arisaig | 0.04 – 0.44 | 0.11 (0.09) |
| 8. Bailey Brook | 0.03 – 4.91 | 0.25 (0.66) |
| 9. Barrios Beach Tracadie | 0.006 – 0.95 | 0.06 (0.02) |
| 10. Caribou Ferry | 0.13 – 1.06 | 0.41 (0.25) |
| 11. Inverness | 0.02 – 0.21 | 0.11 (0.06) |
| 12. Judique Baxter's Cove | 0.02 – 0.31 | 0.12 (0.08) |
| 13. Pictou Landing | 0.09 – 2.26 | 0.35 (0.49) |
| 14. Pleasant Bay | 0.02 – 0.28 | 0.12 (0.09) |
| 15. Skinners Cove | 0.02 – 15.30 | 0.81 (2.97) |
| 16. Battery Point | 0.06 – 0.95 | 0.30 (0.30) |
| 17. Centreville | 0.09 – 1.11 | 0.50 (0.34) |

| SCH | mPEL-Q range in SCH sediment samples | Average mPEL-Q per SCH (+/- SD) |
|---|---|---|
| 18. Clark's Harbour | 0.11- 13.41 | 1.08 (2.70) |
| 19. Delap's Cove | 0.05 – 8.82 | 0.60 (2.00) |
| 20. Fox Point | 0.48 – 10.67 | 4.10 (3.78) |
| 21. Hampton | 0.05 – 0.54 | 0.13 (0.12) |
| 22. Hunts Point | 0.04 – 0.42 | 0.15 (0.10) |
| 23. Little Harbour Shelburne | 0.06 – 9.53 | 0.89 (2.50) |
| 24. Little River Yarmouth | 0.03 – 0.18 | 0.10 (0.06) |
| 25. Moose Harbour | 0.05 – 5.22 | 1.40 (1.73) |
| 26. Pinkney's Point | 0.04 – 1.42 | 0.16 (0.31) |
| 27. Sandford | 0.04 – 0.30 | 0.11 (0.05) |
| 28. South Side | 0.03 – 0.48 | 0.21 (0.17) |
| 29. Stoney Island | 0.02 – 1.09 | 0.11 (0.22) |
| 30. Westport | 0.05 – 0.97 | 0.52 (0.28) |
| 31. Yarmouth Bar | 0.03 – 0.15 | 0.06 (0.03) |

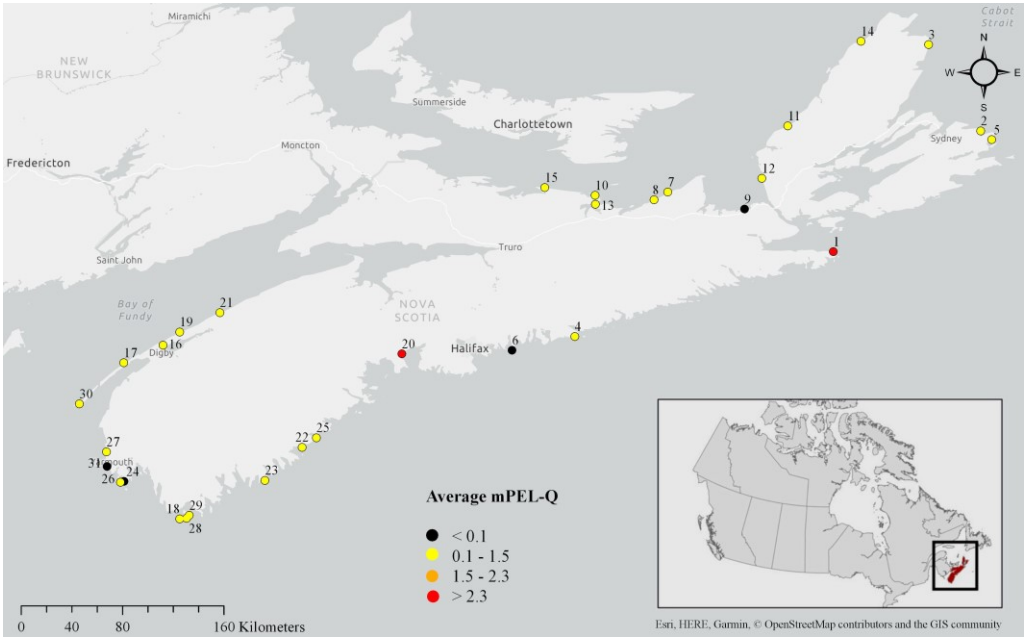



**Figure 4.3** Spatial distribution of average mPEL-Q values across SCHs in Nova Scotia (Inset map of Canada was produced by DMTI™).

Long et al. (1998) established that aquatic sites with an average mPEL-Q >1.0 can be classified as high priority for immediate clean-up actions. This is a similar concept to applying target ecological hazard quotients of 1.0 in ERAs (Walker et al., 2015a). Based on this classification, Canso (SCH 1) in the Eastern region, and Clark's Harbour (SCH 18), Fox Point (SCH 20) and Moose Harbour (SCH 25) in the Southern region, are the SCHs that may require high priority measures (Fig. 4.4). These results are consistent with the previous ERA conducted by Zhang et al. (2019b), where Canso (SCH 1), Clark's

Harbour (SCH 18) and Fox Point (SCH 20) showed the highest average mPEL-Q values. They also align with the previous PAHs characterization (Davis et al., 2018), where Canso (SCH 1) and Fox Point (SCH 20) had the highest mean PAH concentrations in sediment.

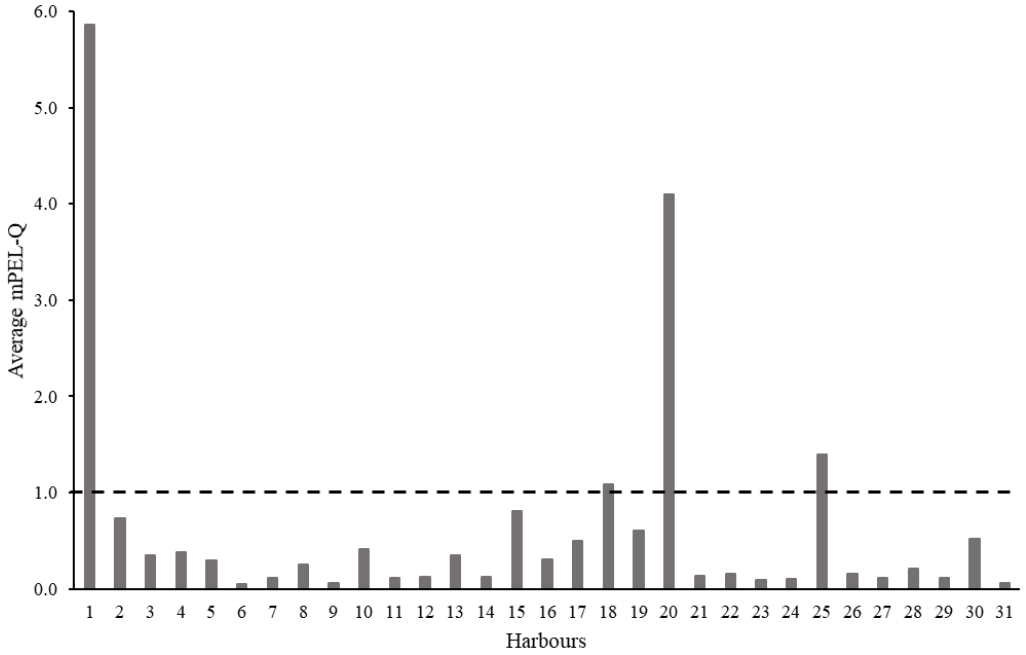



**Figure 4.4** Distribution of average mPEL-Q values in SCH sediments. Dashed horizontal line represents average mPEL-Q >1.

### *4.3.2 Frequency and magnitude of exceedances*

#### *4.3.2.1 Total organic carbon (TOC)*

TOC is considered a sediment toxicity modifying factor as it can alter contaminant partitioning and bioavailability (Simpson and Kumar, 2016). Mean TOC values per SCH varied from 0.5 to 5.41%, with an average of 1.95% across the SCHs. Elevated sediment TOC due to organic enrichment is generally associated with historical sewage inputs, which may create hypoxic sediments and limit the diversity of benthic organisms (Hartnett et al., 1998; Gray et al., 2002; Walker et al., 2015a). In a global study, Hyland et al. (2005) determined that sediment TOC concentrations higher than 4% are associated with a decline in benthic species richness. An apparent effect threshold (AET) of 15.1%

for TOC was established by Barrick et al. (1988). The Ontario Ministry of Environment has established a lowest effect level (LEL) and a severe effect level (SEL) for TOC in sediments of 1% and 10%, respectively (OMOE, 2008). While approximately 80% of the mean TOC concentrations across the SCHs exceeded this LEL, none of the mean SCH sediment concentrations of TOC exceeded the SEL or the AET.

#### *4.3.2.2 Petroleum hydrocarbons (PHCs)*

Atlantic RBCA sediment screening levels for modified TPH (Gas), modified TPH (Fuel) and modified TPH (Lube) were adjusted in each SCH sediment sample based on TOC percentages, using 1% as a default when the TOC values were either not reported or lower than 1%. Thus, each SCH sediment sample has its own sample-specific screening level. A brief description, scope and references to the standardized analytical methods used to determine unadjusted PHC screening levels (i.e., aliphatic fraction forensics) are included as supplementary materials (Appendix B). Descriptive summary statistics for these data, including mean and range TOC values, mean and range for TOC-adjusted screening levels per SCH, and the specific number and percentage of TOC-adjusted screening level exceedances for all SCHs, are included as supplementary materials (Appendix B). For comparative purposes, the overall degree of difference was determined for each SCH, wherein a single mean sediment concentration was calculated for each PHC category (i.e., gas, fuel, lube), for each SCH, which was then divided by the corresponding average TOC-adjusted Atlantic RBCA screening level for the SCH. Results were compared to mean values and degrees of difference calculated by Mora et al. (2022) during the initial characterization study, to see if there were any changes to the outcomes of that study due to the use of TOC-adjusted sediment screening levels (Fig. 5a-b).

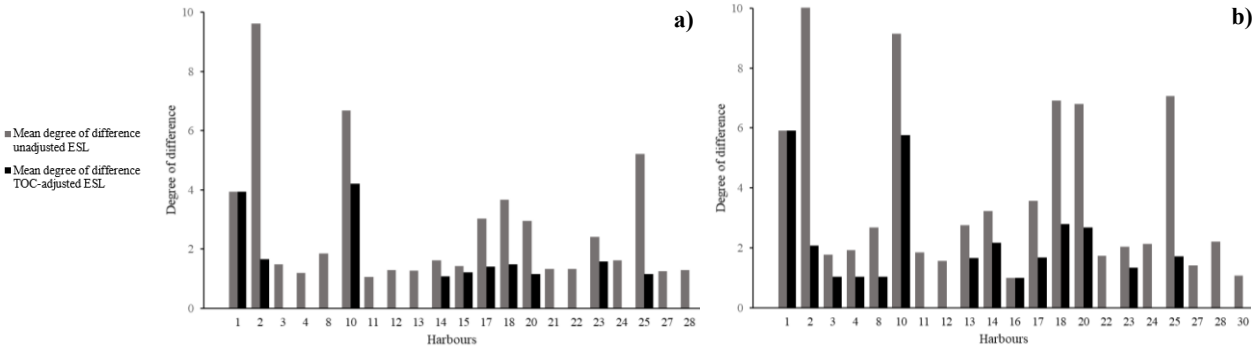



**Figure 4.5a-b** Mean degree of difference for modified TPH (Fuel) (a) and modified TPH (Lube) (b) across SCHs [using default Atlantic RBCA screening levels (grey bars) and TOC-adjusted Atlantic RBCA screening levels (black bars)].

levels, 21 SCHs (67.74%) showed exceedances of over the modified TPH (Fuel) screening level, with an average degree of difference of 2.64 (Mora et al., 2022). When using TOC-adjusted Atlantic RBCA screening levels, only 10 SCHs (32.25%) had exceedances, with an average degree of difference of 1.89. For modified TPH (Lube), Mora et al. (2022) also found screening level exceedances in 21 SCHs (67.74%), with an average degree of difference of 3.72, when using the default unadjusted screening levels. When using TOC-adjusted screening levels, the number of SCHs with exceedances was reduced to 14 (45.16%) and the average degree of difference was 2.28. The modified TPH (Gas) fraction was not included in this analysis as there were essentially no exceedances over the unadjusted sediment screening level in any of the assessed SCHs.

Each sediment sample was evaluated for 8 PHC classifications, meaning each sample can have exceedances for multiple categories. The following exceedances and percentages were calculated for each category and are not a composite of the total number of samples. Out of 528 PHC sediment samples across all SCHs, 115 (21.7%) presented exceedances over TOC-adjusted sediment screening levels for modified TPH (Fuel), 188 (35.6%) for modified TPH (Lube) and 37 (7%) for TPH. The modified TPH (Gas) range only had a single exceedance in the Southwest region (Hampton). The region with the highest percentage of exceedances for modified TPH (Fuel) and TPH was the Eastern region (25% and 16.6% respectively), while modified TPH (Lube) exceedances were highest in the Southwest region (38.3%).

Spatial distribution of the relative frequency of exceedances (i.e., percentage of samples within a SCH that were above screening levels) was also evaluated as part of the risk evaluation. For instance, a relative frequency of 42% for Glace Bay (SCH 2) would indicate that 11 out of the 26 TPH samples in this SCH presented exceedances. The mean relative frequency of exceedance for modified TPH (Fuel) was 39%. There were only 2 SCHs that had 100% of exceedances in all their samples, Canso (SCH 1) in the Eastern Region and Caribou Ferry (SCH 10) in the Gulf Region (Fig. 4.6). For modified TPH (Lube), the average relative frequency of exceedance was 49%. Canso (SCH 1) and Caribou Ferry (SCH 10) also had 100% of samples with exceedances for this parameter, along with Fox Point (SCH 20) in the Southwest region (Fig. 4.7). For TPH, the average relative frequency of exceedance was 21%. The highest percentage of TPH samples with exceedances was 44% in Caribou Ferry (SCH 10) (Fig. 4.8). A breakdown of relative frequency of exceedances per SCH is included as supplemental material (Appendix B).

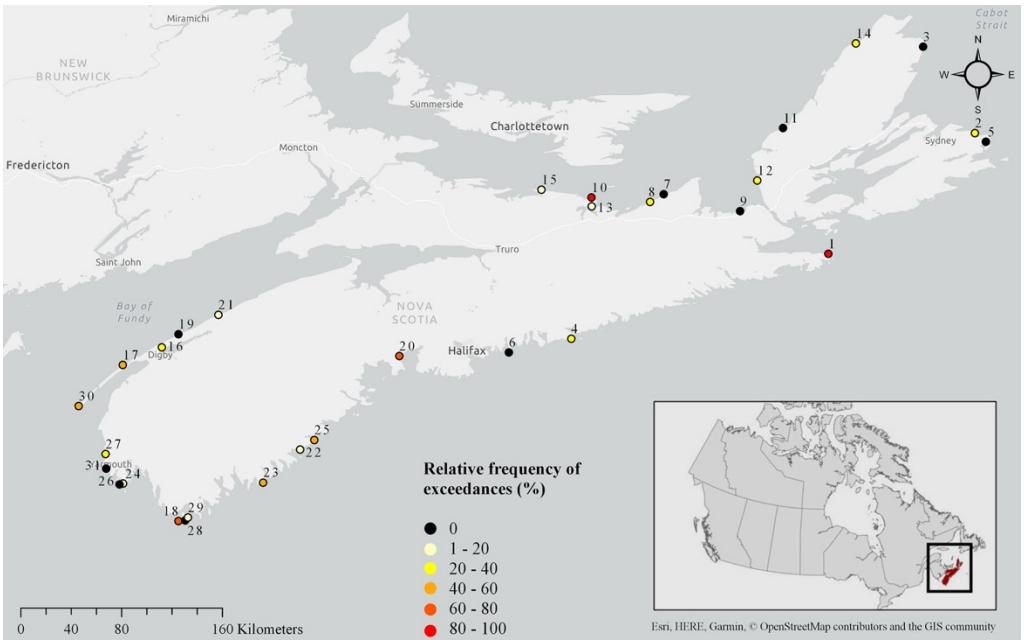



**Figure 4.6** Relative frequency of exceedances per SCH for modified TPH (Fuel) using adjusted Atlantic RBCA screening levels.

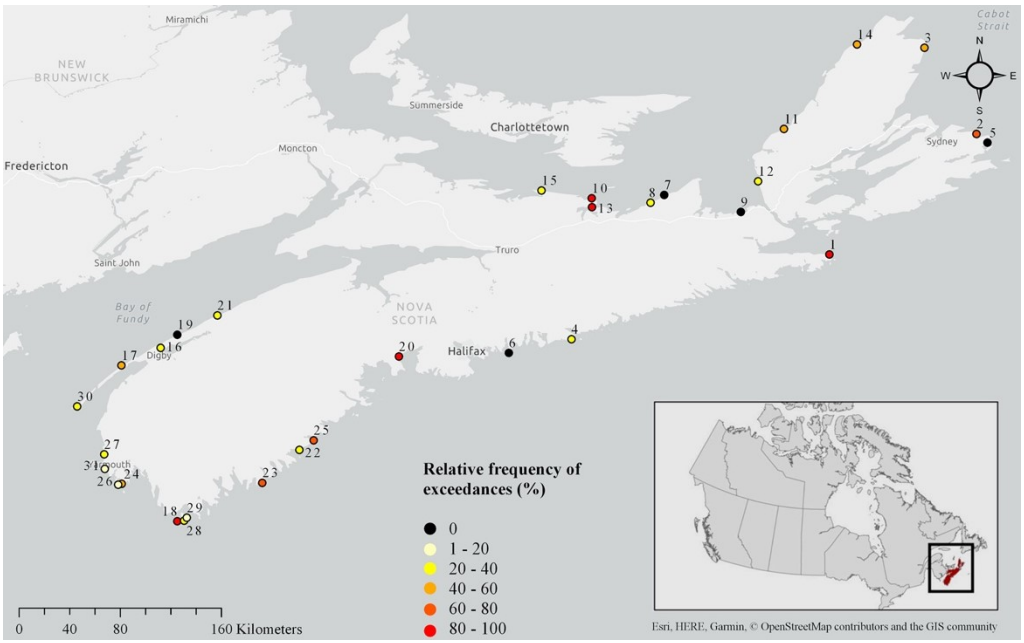



**Figure 4.7** Relative frequency of exceedances per SCH for modified TPH (Lube) using adjusted Atlantic RBCA screening levels.

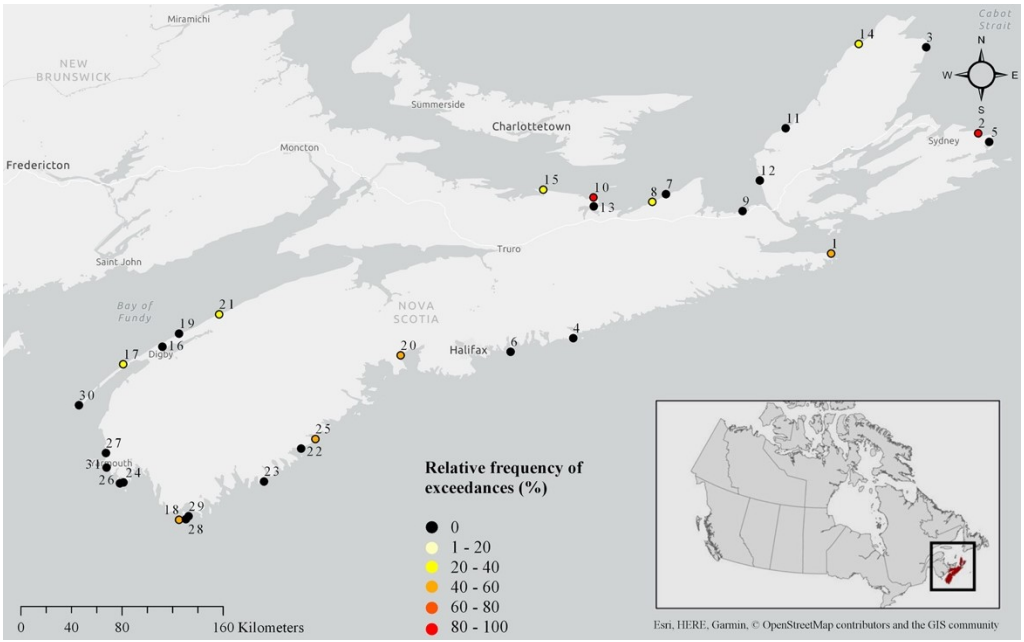



**Figure 4.8** Relative frequency of exceedances per SCH for TPH using Atlantic RBCA screening levels.

### *4.3.2.3 Polycyclic aromatic hydrocarbons (PAHs)*

The overall number and frequency of exceedances for individual PAHs are presented in Table 4.5. The three individual PAHs with the highest frequency of exceedances were

anthracene, fluoranthene and phenanthrene at 15.3, 13.6 and 12.6%, respectively. The region with the highest number of overall exceedances was the Eastern region, where 19.5% of all sediment samples exceeded PELs. Relative frequency of individual PAH exceedances in SCHs is included as supplementary material (Appendix B). Canso (SCH 1) in the Eastern region and Fox Point (SCH 20) in the Southwestern region had the highest relative frequency value, with 75% of sediment samples exceeding PAH SGQs. These results are consistent with Davis et al. (2018), which provides a more detailed analysis of PAHs in SCH sediments.

**Table 4.5** Sediment quality guideline (SQG) exceedances for petroleum hydrocarbons (PHCs), polycyclic aromatic hydrocarbons (PAHs), metals and polychlorinated biphenyls (PCBs) in SCHs.

| Parameter | SGQ (mg/kg) | Number of exceedances (%) |
|---|---|---|
| *Petroleum hydrocarbons (PHCs) (n = 528)* | | |
| Modified TPH (Gas) | 15 | 1 (0.2) |
| Modified TPH (Fuel) | 25 | 115 (21.7) |
| Modified TPH (Lube) | 43 | 188 (35.6) |
| TPH | 500 | 37 (7.0) |
| *Polycyclic aromatic hydrocarbons (PAHs) (n = 580)* | | |
| 2-Methylnaphthalene | 0.201 | 31 (5.3) |
| Acenaphthene | 0.0889 | 42 (7.2) |
| Acenaphthylene | 0.128 | 17 (3.0) |
| Anthracene | 0.245 | 89 (15.3) |
| Benzo(a)anthracene | 0.693 | 65 (11.2) |
| Benzo(a)pyrene | 0.763 | 47 (8.1) |
| Chrysene | 0.846 | 68 (11.7) |
| Dibenz(a,h)anthracene | 0.135 | 29 (5.0) |
| Fluoranthene | 1.494 | 79 (13.6) |
| Fluorene | 0.144 | 55 (9.5) |
| Naphthalene | 0.391 | 13 (2.2) |
| Phenanthrene | 0.544 | 73 (12.6) |
| Pyrene | 1.398 | 62 (10.7) |
| *Metals (n = 576)* | | |
| As | 41.6 | 2 (0.4) |
| Cd | 4.2 | 0 (0.0) |
| Cr | 160 | 1 (0.2) |
| Cu | 108 | 11 (1.9) |
| Hg | 0.7 | 1 (0.2) |
| Ni | 42.8 | 5 (0.9) |
| Pb | 112 | 16 (2.8) |
| Zn | 271 | 9 (1.6) |
| *Polychlorinated biphenyls (PCBs) (n = 531)* | | |
| Total PCBs | 0.189 | 6 (1.1) |

#### *4.3.2.4 Metals*

PEL exceedances for metals in SCH sediments were considerably lower than for PHCs and PAHs. Table 4.5 shows the overall number and frequency of exceedances for metals. Pb, Cu and Zn had the highest frequency of exceedances (2.8, 1.9 and 1.6%, respectively). The Eastern region had the highest percentage of exceedances, with 3%. Relative frequency of metal SQG exceedances in SCHs is included as supplementary material (Appendix B). The highest relative frequencies were found in Canso (SCH 1) in the Eastern region and Clark's Harbour (SCH 18) in the Southwest region, with 17.7 and 6.3%, respectively. For a more detailed evaluation of exhaustive breakdown of metal SQG exceedances in the assessed SCHs, refer to Zhang et al. (2019a).

#### *4.3.2.5 Total polychlorinated biphenyls (PCBs)*

Across all assessed SCHs, there were only six PEL exceedances for PCBs (Table 4.5). Two of these exceedances occurred in the Eastern region (SCH 2) and four occurred in the Gulf region (SCH 8 and SCH 14). The degree of difference for PEL exceedances ranged from 1.2 to 1.9, averaging 1.4. The relative frequency of PCB SQG exceedances in the assessed SCHs is included as supplementary material (Appendix B). Glace Bay (SCH 2) in the Eastern region and Bailey Brook (SCH 8) in the Gulf region had the highest frequency of exceedance, at 7.1%. These results are consistent with the previous characterization conducted by Mora et al. (2022).

### *4.3.3 Potential ecological risk of contaminants in SCHs*

Although PAHs are some of the most ubiquitous contaminants in aquatic environments, they are of particular concern since they may bioaccumulate in food chains and some PAH compounds have been identified as mutagenic and carcinogenic (Fang et al., 2012; Stout et al, 2015; Davis et al., 2018). Metals in aquatic environments are also ubiquitous and have many diverse sources. Some metals in marine sediments may accumulate in biota and affect food webs, and some are of concern given their high toxicity to aquatic life (Bastami et al., 2015; Walker and Grant, 2015; Zhang et al., 2019a).

PCBs have a high affinity for adipose tissue and can bioaccumulate and biomagnify in aquatic food webs, which may lead to various types of adverse effects including liver, kidney, neurological and endocrine effects in aquatic organisms (Walker et al., 2013b; Faroon and Ruiz, 2016; Mora et al., 2022).

Longer chain PHCs like those which are present in modified TPH (Fuel) and modified TPH (Lube) tend to have a limited bioavailability to aquatic organisms given their low water solubility and inability to cross cell membranes (USEPA, 2017). However, they can still impact biota through physical effects like smothering, creation of anoxic areas or coating of foraging zones (Mendelssohn et al., 2012). The screening level of 500 mg/kg for PHCs established by Atlantic RBCA accounts for some of these physical effects in addition to direct toxicity (Atlantic PIRI, 2021).

A study conducted by Meloche and McDonald (2018) identified inadequate maintenance activities, poor wharf infrastructure, debris, low quality fill and stormwater discharge as the main sources of the contaminants of concern in SCHs. These sources increase the presence of PAHs, metals, PCBs and PHCs in SCH sediments primarily through leaching, groundwater transport and land runoff.

Canso (SCH 1) in the Eastern region had the highest average mPEL-Q (5.86), while also showing some of the highest relative frequencies of exceedance and degree of difference for modified TPH (Fuel), modified TPH (Lube) and TPH. Fox Point (SCH 20) had the second highest mPEL-Q (4.1). Like Canso (SCH 1), Fox Point also showed high frequency of exceedance and degree of difference for all PHCs categories but with lower frequencies and smaller magnitudes than Canso.

Caribou Ferry (SCH 10) in the Gulf region was the SCH with the most exceedances for all three PHCs categories, and also showed the highest degree of difference for PHCs. However, its average mPEL-Q shows low risk for the other three contaminants classes that were evaluated (0.41). This study determined that Canso (SCH 1) and Fox Point

(SCH 20) present the highest ecological risk for the four classes of contaminants that were evaluated in SCH sediments.

This study was limited to only including classes of contaminants previously analyzed in MSSPs. However, they align with the CSM from Meloche and McDonald (2014) and have been identified as some of the most common chemical groups in sediment contamination (Morales-Caselles et al., 2017; Dell'Anno et al., 2021; USEPA, 2022). As MSSPs focused on sampling and analyzing the main contaminants of concern for harbours, other compounds may not be known contaminants used in SCHs. There may be some contaminants in SCHs missed from this study, but it would be unlikely to detect them in most SCHs and, therefore, not a major limitation. Nevertheless, studies of other classes of contaminants such as tributyltin (used as a biocide in marine paints), nutrients, organochlorinated pesticides, pharmaceutical drugs (antibiotics), and other emerging contaminants are recommended for future research in SCH sediments, as some SCHs can be located close to aquaculture facilities and other industrial activities (Morales-Caselles et al., 2016; Justine et al., 2016; USEPA, 2022).

### 4.4 Conclusion

Overall, most SCHs show a negligible to low potential for ecological risk to marine biota. PAHs, metals, PCBs and PHCs had a wide variation in sediment concentrations, likely due to sample collection that extended over 17 years and across 31 independent SCHs that are influenced by a variety of contaminant sources to varying degrees. Sediment characterization and risk evaluation studies like this one provide a historical overview of SCH environmental quality in Nova Scotia and can influence decisions involving these SCHs in the future. Risk evaluation results were consistent with those from previous studies (Davis et al., 2018; Zhang et al., 2019a; Zhang et al., 2019b).

No risk SCHs would not need any further actions. While urgent action is not needed, monitoring is recommended for low risk SCHs to confirm that sediment contamination is not increasing, and to potentially identify and control sources of contamination. For high

risk SCHs (as shown by higher value for average mPEL-Q and considerable PHC screening level exceedances), a full ecological risk assessment is recommended (including additional SCH sediment sampling to determine the spatial extent of sediment contamination) to determine if remediation actions should be implemented. While this study is not a full ecological risk assessment, it provides a preliminary overview of potential ecological risks in the subject SCHs. Considering that this evaluation primarily comprised a "screening" of sediment contamination in SCHs, it is recommended to integrate this study with other components such as coastal hydrodynamics, habitat type and resident biota to create a more holistic assessment of SCH environmental quality. Conducting biota tissue sampling and analytical programs is also suggested within the SCHs that presented a higher potential ecological risk. Consideration should be given to testing target species to verify the biological matrix response to contaminated waters, including those with low value or even no contamination.

Comprehensive studies in SCHs are important to determine sediment quality and potential sources of harbour contamination. Results like those obtained from this research can inform harbour authorities about historical contamination and current environmental quality of SCHs, so future risk-management options can be developed and prioritized to comply with established environmental quality standards. Since most SCHs tend to have similar biophysical features and activities, similar monitoring and mitigation actions can likely be applied across most SCHs.

# CHAPTER 5 FINDINGS, MANAGEMENT RECOMMENDATIONS AND CONCLUSIONS

## 5.1 PHCs characterization key findings

This research found that 38% and 49% of all PHC samples presented exceedances for diesel and lube oil, respectively. These results were expected as fuel and lube oil hydrocarbons have higher densities and longer persistence at contaminated sites. The presence of these PHC classifications also aligns with activities commonly carried out in SCHs. While contamination sources were not identified as part of this study, potential origins can include spills during refueling or diesel transportation, improper fuel storage, as well as inadequate storage of fuel and lubricant used for vessels and equipment maintenance.

Only 7% of all samples exceeded 500 ppm, threshold where benthic impairment and physical impacts from fouling are observed, showing low risk of impacts to biota. BTEX and gasoline only had one or two exceedances out of the 528 samples analyzed in the study. It is more uncommon to find high concentrations of these compounds in sediments, as they are highly volatile and evaporate quickly after their release. Glace Bay (SCH 2) in the Eastern region and Caribou Ferry (SCH 10) in the Gulf region had the highest concentrations for modified TPH (Fuel), modified TPH (Lube) and TPH, presenting the only two exceedances for TPH in single mean values per SCH. Overall, SCHs in the Southwest region appears to be the most influenced by PHCs presence.

## 5.2 PCBs characterization key findings

PCBs do not pose high risk to biota since only six samples exceeded PEL and 25% of them exceeded ISQG, which is a more conservative guideline value. Additionally, 5% of all samples had concentrations above CEPA Disposal at Sea Guidelines. It has been hypothesized that PCBs could be originating from fish plants in proximity to SCHs (R. Mroz, personal communication, October 5, 2021). When looking at single mean values per SCHs, there were no exceedances of PEL or CEPA Disposal at Sea Guidelines. Glace Bay (SCH 2) in the Eastern region, Bailey's Brook (SCH 8) and Pleasant Bay (SCH 14)

in the Southwest region, and Clark's Harbour (SCH 18), Moose Harbour (SCH 25), South Side (SCH 28) and Stoney Island (SCH 29) had mean total PCB concentrations in sediment which showed exceedances over ISQG. While ISQGs represent the lower effect level for effects to biota, exceedances of PCBs ISQG do require further assessments given their toxicity and bioaccumulating characteristics (J. Berry, personal communication, October 5, 2021). As PHCs, the Southwest region was the one that presented the most exceedances for total PCBs.

### 5.3 Ecological risk evaluation key findings

When using the mean probable effect level quotient (mPEL-Q) methodology, most SCHs showed low ecological risk to marine biota, with only two SCHs presenting high risk. Canso (SCH 1) in the Eastern region had the highest average mPEL-Q (5.8), while also showing some of the highest relative frequencies of exceedance for PHCs. The second highest mPEL-Q (4.10) was found Fox Point (SCH 20) in the Southwest region. It also had a large number of PHCs exceedances but with lower frequencies and smaller magnitudes compared to Canso (SCH 1). Clark's Harbour (SCH 18) in the Southwest region had the third highest mPEL-Q (1.00), being on the limit for clean up prioritization (Long et al., 2000)

Caribou Ferry (SCH 10) in the Gulf region was the SCH with the most PHCs exceedances for all categories. However, its mPEL-Q shows low risk (0.41). It was determined that Canso (SCH 1) and Fox Point (SCH 20) present the highest ecological risk for the four classes of contaminants evaluated. Further sediment sampling is recommended for SCHs with highest risk to verify the spatial extent of sediment contamination.

### 5.4 Management implications and recommendations

Recommendations presented on this section are based on key findings for the PHC and PCB characterization and the ecological risk evaluation. Results were consistent with previous studies (Davis et al., 2018; Zhang et al., 2019a; Zhang et al., 2019b). Similar to prior studies of Nova Scotia SCHs, there was a significant variation in distribution PHCs

and PCBs throughout SCH sediment, which could be attributed to sample collection that extended over 17 years and across 31 independent SCHs and dredging activities in certain SCHs that inhibit long-term buildup of compounds in sediments.

Any measures taken in SCHs should be aligned with the recommendations made by the Standing Committee on Fisheries and Oceans (2019). Adequate and regular dredging was recommended as part of their report, which would indicate regular sediment sampling and testing will be needed to comply with CEPA Disposal at Sea Guidelines. There are 3 SCHs in Nova Scotia that should be prioritized by SCH managers Canso (SCH 1) Glace Bay (SCH 2) and Fox Point (SCH 20), as there may be historical or current sources of contamination in the surrounding areas. Other lines of evidence apart from sediment quality such as underwater benthic invertebrate surveys and resident biota tissue sampling can also be used to delineate the degree of contamination around these SCHs.

Other sediment physicochemical components should also be monitored on par with classes of contaminants. There is a correlation between benthic taxonomy and sediment composition. Benthic communities can be influenced by sediment grain size distribution and TOC concentrations, as contaminants would be less bioavailable for them in fine-grained sediments (Romano et al., 2017). On the other hand, it has been observed that an overabundance of TOC can affect benthic richness, biomass and abundance more than contaminant concentrations (Hyland et al., 2005). Similar risk assessment in SCHs suggested a low to moderate risk to benthic invertebrates. However, impacts were not correlated with contamination but most likely caused by habitat alteration given the presence of debris (Meloche and McDonald, 2018).

It is also recommended to prioritize the removal of debris (e.g., batteries, engines, fuel tanks, nets/traps, cans, etc.) from SCHs as it can physically affect biota and could also seep potential contaminants into the environment. A refuse removal could be implemented in places deemed to be severely affected by debris (large presence of hazardous rubble during reconnaissance activities by divers). This program could include the mobilization of community boats, barge, and excavators, as well as divers. In BC, this

type of program has been intermittently supported by Canadian Coast Guard Vessels of Concern Program (McManus and Hamilton, 2019).

There are actions that could be taken in all SCHs regardless their risk to ensure that pollution levels stay below SQGs and minimize the future contamination in the area. These measures include:

- Following best practices for transportation and fuel storage;
- Debris removal with a focus on hazardous items;
- Ensuring storage location for fuel oil (most prevalent one in the characterization) must not be close to water;
- Use of renewable energy in SCHs facilities, such as solar and wind energy;
- Smaller vessels could potentially be electrically powered;
- Risk communication and engagement with SCH users.

In the past few years, SCH sediment investigation program was conducted in Newfoundland and Labrador. Some recommendations based on lessons learned from that study could be applied in Nova Scotia (J. Berry, personal communication, October 5, 2021). Before carrying out the study, the sampling program was standardized so results could be input into a database. While sampling design would need to be modified and homogenized, the development of a management database is still possible for Nova Scotia. This database would include sources of contamination, contaminants of concern, summary of environmental data collected, summary of human health risk assessments and summary of ecological risk assessments. Sampling design also needs to diversify the location of stations, placing them around the areas where boats are stored too, not only around the wharf.

Lastly, public engagement is key to identifying and minimizing sources of contamination in SCHs. Programs for local SCHs users with a focus on commercial users and programs to support community and harbour authority initiatives will inform decision-makers about the health and safety concerns from the community. Environmental education through

engagement programs will involve the community in taking care of SCHs and implementing best industry practices, such as appropriate storage and disposal options.

### 5.5 Conclusions

This research provides an overall holistic conclusion to previous studies regarding potential contaminants of concern in SCHs in Nova Scotia and provides an overview of historical and current conditions of sediments in SCHs. Comprehensive studies in SCHs are important to determine sediment quality and potential sources of harbour pollution. Results like those obtained from this research can inform harbour authorities about historical contamination and current environmental quality of SCHs, so future risk-management options can be developed and prioritized to comply with established environmental quality standards. Since most SCHs tend to have similar activities and biophysical features, similar monitoring and mitigation actions can likely be applied across most SCHs.

Given the outcomes of the ecological risk evaluation and the supporting lines of evidence, it was concluded that future actions in most SCHs in Nova Scotia were not necessary to conduct at this time. There is no current need to proceed with a new detailed testing program or reclassify the risk of the aquatic sites. Developing and implementing a risk management strategy, as well as subsequent monitoring is not required either.

Toxicity benchmarks presented in this thesis need to also be continuously revisited and updated, since they are based on empirical toxicity data, predictive models and criteria obtained from different jurisdictions. McCarty et al. (2018) stated that regular updates in data interpretation and analysis, including ecotoxicity data, physicochemical properties, and contaminant fate and behaviour is necessary to improve existing guidelines and regulatory processes. They ought to be iterative documents that should be reviewed as new studies are conducted and new data is published. An example of this continuous improvement process is Atlantic RBCA. While conducting the characterization portion of the research, version 3 (Atlantic PIRI, 2021) was used as it was the most recent version. However, Atlantic PIRI published an updated version in July 2021 (Atlantic PIRI, 2021).

While concentrations did not change, the definitions to refer to each PHC classification were modified. The characterization and ecological risk evaluation were updated accordingly to reflect these changes, and to present the latest version of regulatory guidelines.

For SCHs that showed higher risk, future monitoring is recommended to identify potential sources of contamination. Integrating this sediment screening with other studies such as benthic taxonomy studies or biota tissue sampling would provide a better overview of the extent of contaminations to organisms. Understanding the behaviour of a contaminant in biotic and abiotic components helps to conduct an adequate assessment of the site and determine best remedial management actions to address environmental impacts. Future research in SCHs needs to also consider regional background factors like habitat type, resident biota and coastal hydrodynamics to better understand the transport and fate of contaminants in aquatic environments and plan environmental protection measures accordingly.

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**Chapter 2 – Background**

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**Chapter 5 – Findings, management recommendations and conclusions**

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## APPENDIX A Supplementary material for the spatiotemporal characterization of petroleum hydrocarbons and polychlorinated biphenyls in small craft harbour sediments in Nova Scotia, Canada

**Table A1** SCHs coordinates with decimal degrees

| SCH | Longitude | Latitude |
|---|---|---|
| 1. Canso | -60.997585 | 45.338824 |
| 2. Glace Bay | -59.950115 | 46.195538 |
| 3. Neil's Harbour | -60.320046 | 46.80772 |
| 4. Owls Head | -62.831834 | 44.736155 |
| 5. Port Morien | -59.873003 | 46.132883 |
| 6. Three Fathom Harbour | -63.276634 | 44.638822 |
| 7. Arisaig | -62.171611 | 45.761757 |
| 8. Bailey Brook | -62.269015 | 45.706602 |
| 9. Barrios Beach Tracadie | -61.626806 | 45.640928 |
| 10. Caribou Ferry | -62.686965 | 45.738184 |
| 11. Inverness | -61.319194 | 46.230335 |
| 12. Judique Baxter's Cove | -61.502867 | 45.858399 |
| 13. Pictou Landing | -62.684431 | 45.675216 |
| 14. Pleasant Bay | -60.799764 | 46.830502 |
| 15. Skinners Cove | -63.044169 | 45.793522 |
| 16. Battery Point | -65.752855 | 44.675289 |
| 17. Centreville | -66.031923 | 44.550735 |
| 18. Clark's Harbour | -65.634936 | 43.443701 |
| 19. Delap's Cove | -65.635427 | 44.76943 |
| 20. Fox Point | -64.058781 | 44.613703 |
| 21. Hampton | -65.34981 | 44.906697 |
| 22. Hunts Point | -64.766494 | 43.951935 |
| 23. Little Harbour Shelburne | -65.029638 | 43.717251 |
| 24. Little River Yarmouth | -66.030364 | 43.710984 |
| 25. Moose Harbour | -64.665207 | 44.018997 |
| 26. Pinkney's Point | -66.055939 | 43.704256 |
| 27. Sandford | -66.155163 | 43.918629 |
| 28. South Side | -65.586231 | 43.446989 |
| 29. Stoney Island | -65.567104 | 43.468048 |
| 30. Westport | -66.346383 | 44.258757 |
| 31. Yarmouth Bar | -66.150732 | 43.815474 |

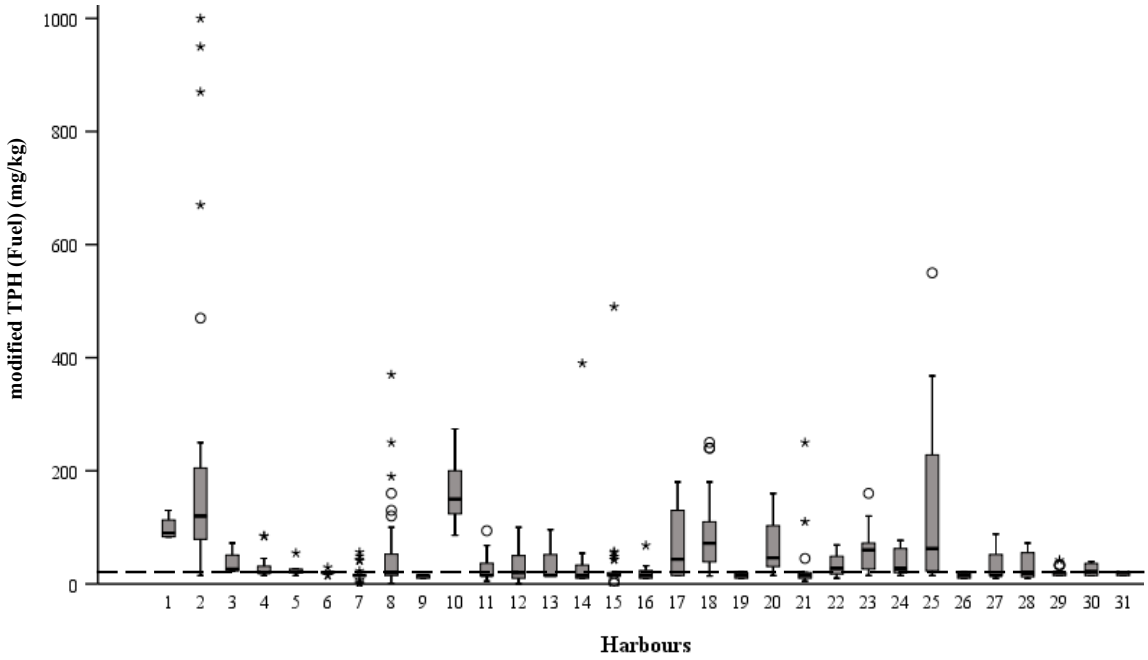


**Figure A1** Distributions of modified TPH (Fuel) concentrations across Nova Scotia SCHs. Horizontal dashed line represents Atlantic RBCA screening level (25 m/kg).

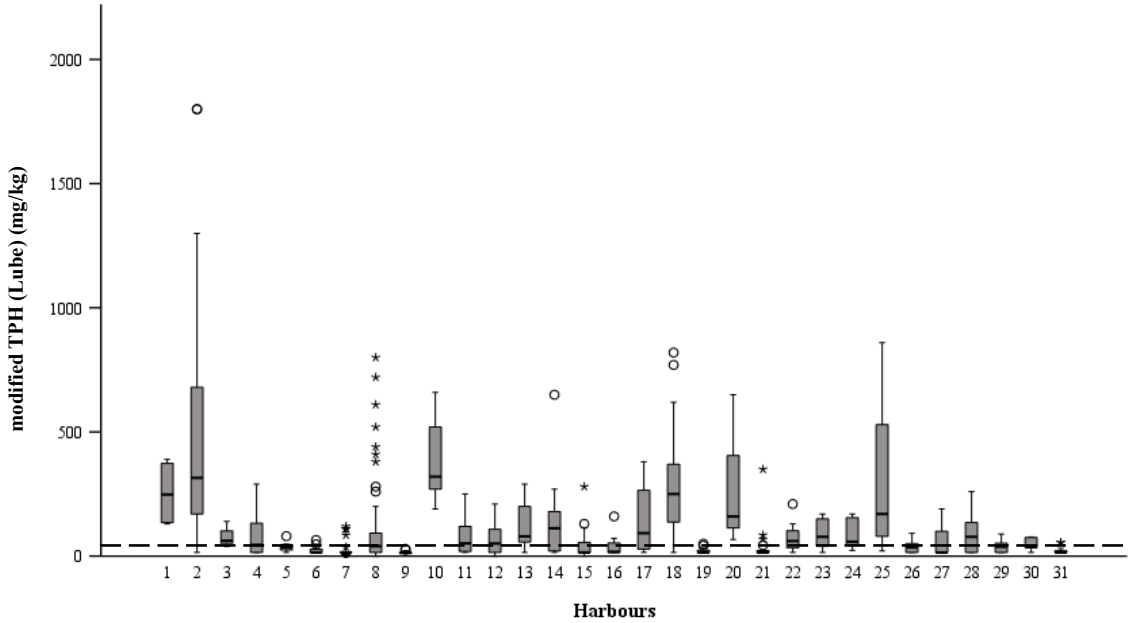


**Figure A2** Distributions of modified TPH (Lube) concentrations across Nova Scotia SCHs. Horizontal dashed line represents Atlantic RBCA screening level (43 mg/kg).

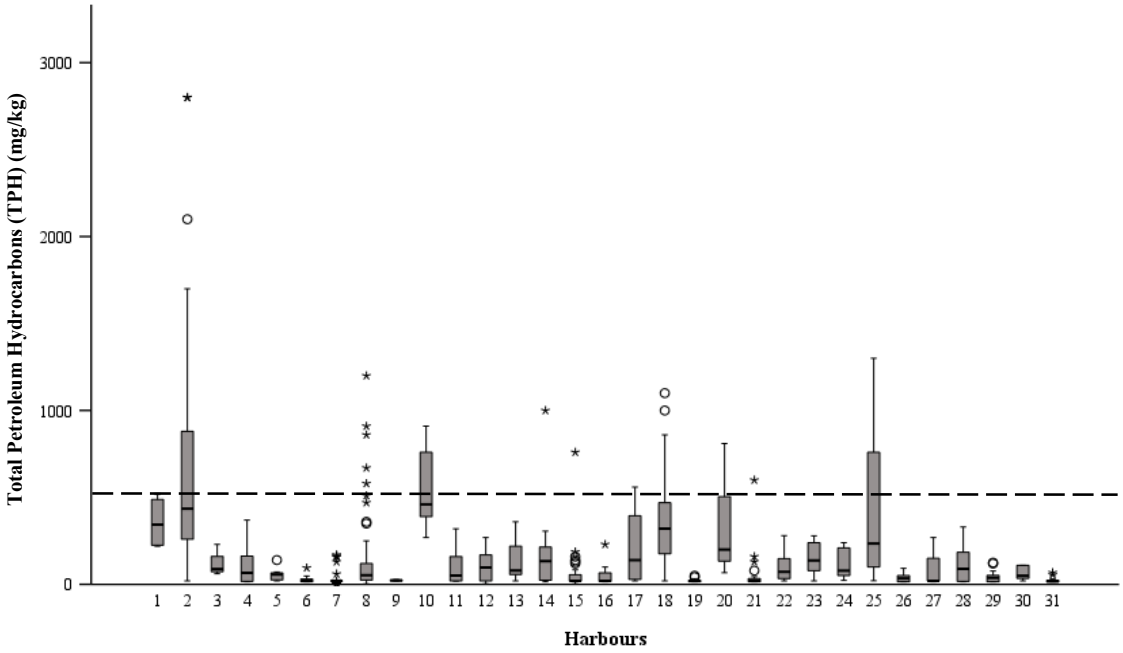


**Figure A3** Distributions of TPH concentrations across Nova Scotia SCHs. Horizontal dashed line represents Atlantic RBCA screening level (500 mg/kg).

## APPENDIX B Supplementary material for the multiple contaminant ecological risk evaluation in small craft harbour sediments in Nova Scotia, Canada

**Table B1** Scientific rationale for petroleum hydrocarbon sediment screening levels used in this study (Atlantic PIRI, 2012; Atlantic PIRI, 2021).

| | |
|---|---|
| **Context** | There are no Canadian federal sediment quality guidelines for petroleum hydrocarbons. In 2012, the Atlantic Risk-Based Corrective Action task group undertook the development of screening levels based on the principles of narcosis and equilibrium partitioning. Results were validated with a toxicity testing program (PETROTOX). |
| **Equilibrium partitioning method** | Surface water screening levels were used to calculate sediment quality screening levels through equilibrium partitioning. This model assumes that toxicity of a compound in sediment is related to the chemical's concentration in porewater. Partitioning behavior of a chemical is linked to the compound's organic-carbon partitioning coefficient ($K_{oc}$) and sediment's fraction organic carbon ($F_{oc}$). This approach is useful for non-polar contaminants like petroleum hydrocarbons. The quantification methodology is as follows: Sediment screening level = surface water screening level ($K_{oc}$)($F_{oc}$). Aquatic chronic and acute endpoints were used to calculate narcosis-based aliphatic sediment quality benchmarks. Sediment screening levels were based on a $F_{oc}$ of 1%. For other $F_{oc}$ values, the screening levels change proportionally, which allows for site-specific adjustments. |
| **PETROTOX** | The PETROTOX model provides predicted exposure and predicted toxicity for petroleum hydrocarbon products to aquatic organisms by applying a target lipid narcosis model. The acute and chronic aliphatic sediment quality benchmark values were back-calculated for each petroleum hydrocarbon range to calculate the final sediment toxicity benchmarks. To validate the calculated benchmarks, laboratory studies were conducted to determine the toxicity of modified TPH (Fuel) (winter diesel) and modified TPH (Lube) (Bunker C) using benthic invertebrates. Results showed that modified TPH screening levels were typically within the range of confidence limits. |
| **Non-narcosis sediment benchmarks** | Other petroleum hydrocarbon effects apart from narcosis can occur in benthic organisms. Adverse effects like physical soiling of organisms and oxygen depletion can take place with the presence of petroleum hydrocarbons. These types of effects are not specific to a petroleum hydrocarbon range but rather the total amount present. As there are no models available for these effects, field studies were used as basis for a total petroleum hydrocarbons sediment benchmark. Based on the weight of evidence from the conducted literature review, a maximum screening level of 500 mg/kg dry weight of sediment was recommended for total petroleum hydrocarbons. |
| **Detection limit considerations** | To avoid problems with false positives during use of screening levels, two analytical laboratories in Atlantic Canada were surveyed to determine the detection limits for petroleum hydrocarbons in sediment. Based on the results, none of the screening levels were set below detection limits. |
| **Conclusions** | Testing results indicated a good agreement between predicted sediment concentration and toxicity, supporting the recommended screening levels. Sediment quality benchmarks obtained through PETROTOX are protective of aquatic species. Accuracy and value of the model were further validated by a strong agreement with toxicity endpoints from laboratory studies. |

References:
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**Table B2** Ranges and mean values for adjusted Atlantic RBCA screening levels, and number and percentage of screening level exceedances per SCH.

| SCH | TOC range (%) | TOC mean (%) | Adjusted modified TPH (Fuel) screening level range (mg/kg) | Adjusted modified TPH (Fuel) screening level mean (mg/kg) | Number of modified TPH (Fuel) exceedances (%) | Adjusted modified TPH (Lube) screening level range (mg/kg) | Adjusted modified TPH (Lube) screening level mean (mg/kg) | Number of modified TPH (Lube) exceedances (%) | Modified TPH screening level (mg/kg) | Number of modified TPH exceedances (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.4-0.6 | 0.5 | 25.0 | 25.0 | 4 (100.0) | 43.0 | 43.0 | 4 (100.0) | 500 | 1 (25.0) |
| 2 | 0.7-73.0 | 7.8 | 25.0-500.0 | 144.5 | 10 (38.4) | 43.0-500.0 | 232.5 | 16 (61.5) | 500 | 11 (42.5) |
| 3 | 0.5-3.30 | 1.5 | 25.0-82.5 | 42.5 | 0 (0.0) | 43-142 | 73.1 | 2 (50.0) | 500 | 0 (0.0) |
| 4 | 0.09-5.1 | 1.5 | 25.0-127.5 | 46.8 | 4 (25.0) | 43.0-219.3 | 80.6 | 5 (31.3) | 500 | 0 (0.0) |
| 5 | 0.2-12.5 | 5.2 | 25.0-312.5 | 132.8 | 0 (0.0) | 43.0-500.0 | 224.8 | 0 (0.0) | 500 | 0 (0.0) |
| 6 | 0.08-6.0 | 1.6 | 25.0-150.0 | 50.0 | 0 (0.0) | 43-258 | 86.0 | 0 (0.0) | 500 | 0 (0.0) |
| 7 | 0.02-6.6 | 1.5 | 25.0-165.0 | 51.5 | 0 (0.0) | 43.0-283.8 | 88.6 | 0 (0.0) | 500 | 0 (0.0) |
| 8 | 0.06-17.0 | 3.1 | 25.0-42.5 | 66.3 | 14 (22.5) | 43.0-500.0 | 110.4 | 17 (27.4) | 500 | 6 (9.7) |
| 9 | 0.3-2.1 | 0.7 | 25.0-52.5 | 48.9 | 0 (0.0) | 43.0-90.3 | 67.0 | 0 (0.0) | 500 | 0 (0.0) |
| 10 | 0.8-2.0 | 1.5 | 25.0-50.0 | 39.7 | 9 (100.0) | 43.0-86.0 | 68.3 | 9 (100.0) | 500 | 4 (44.4) |
| 11 | 0.02-4.9 | 1.8 | 25.0-122.5 | 46.9 | 0 (0.0) | 43.0-210.7 | 80.8 | 9 (40.9) | 500 | 0 (0.0) |
| 12 | 0.01-15.0 | 1.6 | 25.0-375 | 47.2 | 8 (29.6) | 43.0-500.0 | 75.8 | 9 (33.3) | 500 | 0 (0.0) |
| 13 | 0.9-3.2 | 2.2 | 25.0-80.0 | 41.6 | 3 (17.6) | 43.0-137.6 | 71.5 | 14 (82.4) | 500 | 0 (0.0) |
| 14 | 0.01-6.3 | 1.3 | 25.0-157.5 | 37.2 | 6 (31.6) | 43.0-271 | 64.0 | 11 (57.9) | 500 | 1 (3.1) |
| 15 | 0.01-2.9 | 0.7 | 25.0-72.5 | 29.7 | 5 (15.6) | 43.0-124.7 | 51.1 | 8 (25.0) | 500 | 1 (3.1) |
| 16 | 0.1-1.0 | 0.5 | 25.0 | 25.0 | 2 (25.0) | 43.0 | 43.0 | 2 (25.0) | 500 | 0 (0.0) |
| 17 | 0.1-4.6 | 1.9 | 25.0-115.0 | 53.5 | 4 (57.1) | 43.0-197.8 | 92.1 | 4 (57.1) | 500 | 1 (14.3) |
| 18 | 0.1-5.6 | 2.1 | 25.0-140.0 | 61.7 | 14 (63.6) | 43.0-240.8 | 106.1 | 20 (90.9) | 500 | 5 (22.7) |
| 19 | 0.08-3.3 | 1.0 | 25.0-82.5 | 32.3 | 0 (0.0) | 43.0-141.9 | 55.6 | 0 (0.0) | 500 | 0 (0.0) |
| 20 | 0.6-4.9 | 2.4 | 25.0-122.5 | 63.3 | 2 (66.7) | 43.0-210.7 | 108.9 | 3 (100.0) | 500 | 1 (33.3) |
| 21 | 0.03-7.1 | 1.4 | 25.0-177.5 | 41.4 | 3 (15.8) | 43.0-305.3 | 71.2 | 4 (21.1) | 500 | 1 (5.3) |
| 22 | 0.3-4.7 | 1.8 | 25.0-117.5 | 47.3 | 1 (8.3) | 43.0-202.1 | 81.5 | 4 (33.3) | 500 | 0 (0.0) |
| 23 | 0.1-3.4 | 1.1 | 25.0-85.0 | 37.8 | 6 (46.2) | 43.0-146.2 | 65.1 | 9 (69.2) | 500 | 0 (0.0) |
| 24 | 0.7-3.4 | 2.1 | 25.0-85.0 | 40.4 | 2 (18.9) | 43.0-146.2 | 94.9 | 5 (45.5) | 500 | 0 (0.0) |
| 25 | 0.1-19.0 | 5.4 | 25.0-475.0 | 118.7 | 8 (44.4) | 43.0-500.0 | 186.6 | 14 (77.7) | 500 | 5 (27.8) |
| 26 | 0.4-2.6 | 1.4 | 25.0-65.0 | 39.0 | 0 (0.0) | 43.0-111.8 | 67.1 | 2 (11.7) | 500 | 0 (0.0) |
| 27 | 0.06-3.1 | 1.0 | 25.0-77.5 | 35.5 | 8 (38.1) | 43.0-133.3 | 61.2 | 8 (38.1) | 500 | 0 (0.0) |
| 28 | 0.6-6.0 | 2.7 | 25.0-150.0 | 70.3 | 0 (0.0) | 43.0-258.0 | 120.9 | 2 (25.0) | 500 | 0 (0.0) |
| 29 | 0.08-4.4 | 1.2 | 25.0-110.0 | 35.6 | 1 (4.7) | 43.0-189.2 | 61.3 | 4 (19.0) | 500 | 0 (0.0) |
| 30 | 0.2-1.3 | 0.8 | 25.0-32.5 | 27.0 | 3 (50.0) | 43.0-55.9 | 46.5 | 2 (33.3) | 500 | 0 (0.0) |
| 31 | 0.05-1.6 | 0.5 | 25.0-40.0 | 26.5 | 0 (0.0) | 43.0-68.8 | 45.6 | 1 (6.3) | 500 | 0 (0.0) |

**Table B3** Relative frequency of exceedances (%) of petroleum hydrocarbons (PHCs) and individual polycyclic aromatic hydrocarbons (PAHs) per SCH.

| SCH | Modified TPH (Gas) | Modified TPH (Fuel) | Modified TPH (Lube) | TPH* | 2MNa* | ACE* | ACY* | AN* | BaA* | BaP* | CH* | DA* | FLU* | FL* | NA* | PH* | PY* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0 | 100.0 | 100.0 | 25.0 | 16.7 | 58.3 | 50.0 | 100.0 | 100.0 | 91.7 | 100.0 | 83.3 | 100.0 | 75.0 | 16.7 | 91.7 | 91.7 |
| 2 | 0.0 | 38.4 | 61.5 | 42.5 | 37.1 | 21.4 | 7.1 | 28.6 | 7.1 | 7.1 | 7.1 | 7.1 | 17.8 | 21.4 | 7.1 | 39.3 | 10.7 |
| 3 | 0.0 | 0.0 | 50 | 0.0 | 0.0 | 0.0 | 0.0 | 25.0 | 25.0 | 25.0 | 25.0 | 12.5 | 12.5 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 0.0 | 25.0 | 31.2 | 0.0 | 0.0 | 33.3 | 0.0 | 33.3 | 23.8 | 9.5 | 19.1 | 4.7 | 19.1 | 19.1 | 0.0 | 14.3 | 14.3 |
| 5 | 0.0 | 0.0 | 0.0 | 0.0 | 53.3 | 0.0 | 0.0 | 20.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.7 | 6.7 | 0.0 | 20.0 | 0.0 |
| 6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.3 | 0.0 | 3.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.3 | 0.0 | 3.3 | 0.0 |
| 8 | 0.0 | 22.5 | 27.4 | 9.7 | 0.0 | 5.9 | 0.0 | 3.9 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 3.9 | 2.0 | 3.9 | 2.0 |
| 9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 10 | 0.0 | 100.0 | 100.0 | 44.4 | 7.7 | 7.7 | 0.0 | 15.4 | 23.1 | 0.0 | 7.7 | 0.0 | 53.8 | 7.7 | 7.7 | 7.7 | 30.8 |
| 11 | 0.0 | 0.0 | 40.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 12 | 0.0 | 29.6 | 33.3 | 0.0 | 0.0 | 3.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 13 | 0.0 | 17.6 | 82.3 | 0.0 | 5.9 | 5.9 | 0.0 | 11.8 | 5.9 | 5.9 | 5.9 | 5.9 | 11.8 | 11.8 | 5.9 | 11.8 | 11.8 |
| 14 | 0.0 | 31.6 | 57.9 | 3.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 15 | 0.0 | 15.6 | 25.0 | 3.1 | 8.0 | 12.0 | 0.0 | 12.0 | 8.0 | 4.0 | 12.0 | 0.0 | 20.0 | 12 | 4.0 | 12.0 | 12.0 |
| 16 | 0.0 | 25.0 | 25.0 | 0.0 | 0.0 | 0.0 | 0.0 | 33.3 | 33.3 | 11.1 | 33.3 | 0.0 | 33.3 | 11.1 | 0.0 | 33.3 | 33.3 |
| 17 | 0.0 | 57.1 | 57.14 | 14.3 | 0.0 | 10.0 | 10.0 | 50.0 | 30.0 | 10.0 | 40.0 | 0.0 | 50.0 | 30.0 | 0.0 | 60.0 | 30.0 |
| 18 | 0.0 | 63.6 | 90.9 | 22.7 | 0.0 | 4.6 | 4.6 | 36.4 | 36.4 | 27.3 | 45.5 | 4.5 | 31.8 | 9.1 | 0.0 | 4.6 | 36.7 |
| 19 | 0.0 | 0.0 | 0.0 | 0.0 | 5.6 | 5.6 | 0.0 | 11.1 | 11.1 | 5.6 | 11.1 | 5.6 | 5.6 | 11.1 | 5.6 | 11.1 | 5.6 |
| 20 | 0.0 | 66.6 | 100.0 | 33.3 | 50.0 | 50.0 | 66.7 | 100.0 | 100.0 | 83.3 | 100.0 | 83.3 | 83.3 | 83.3 | 0.0 | 100.0 | 83.3 |
| 21 | 5.3 | 15.8 | 21.0 | 5.3 | 6.3 | 0.0 | 0.0 | 10.5 | 0.0 | 0.0 | 6.3 | 0.0 | 6.3 | 6.3 | 0.0 | 6.2 | 0.0 |
| 22 | 0.0 | 8.3 | 33.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.1 | 0.0 | 0.0 | 7.1 | 7.1 |
| 23 | 0.0 | 46.1 | 69.2 | 0.0 | 7.7 | 7.7 | 15.4 | 15.4 | 7.7 | 15.4 | 7.7 | 0.0 | 7.7 | 7.7 | 7.7 | 7.7 | 0.0 |
| 24 | 0.0 | 18.2 | 45.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 25 | 0.0 | 44.4 | 77.7 | 27.8 | 5.3 | 21.1 | 0.0 | 47.4 | 47.4 | 42.1 | 52.6 | 31.6 | 42.1 | 36.8 | 10.5 | 36.8 | 42.1 |
| 26 | 0.0 | 0.0 | 11.7 | 0.0 | 0.0 | 0.0 | 0.0 | 5.6 | 0.0 | 0.0 | 0.0 | 0.0 | 5.6 | 5.6 | 0.0 | 5.6 | 0.0 |
| 27 | 0.0 | 38.1 | 38.1 | 0.0 | 0.0 | 0.0 | 4.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 28 | 0.0 | 0.0 | 25.0 | 0.0 | 0.0 | 0.0 | 0.0 | 33.3 | 11.1 | 0.0 | 11.1 | 0.0 | 11.1 | 11.1 | 0.0 | 11.1 | 11.1 |
| 29 | 0.0 | 4.7 | 19.0 | 0.0 | 0.0 | 4.3 | 0.0 | 4.3 | 4.3 | 0.0 | 4.3 | 0.0 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 |
| 30 | 0.0 | 50.0 | 33.3 | 0.0 | 0.0 | 0.0 | 0.0 | 71.4 | 42.9 | 42.9 | 42.9 | 0.0 | 71.4 | 14.3 | 0.0 | 71.4 | 57.1 |
| 31 | 0.0 | 0.0 | 6.25 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| mean | 0.2 | 26.4 | 40.7 | 7.5 | 6.6 | 8.2 | 5.1 | 21.7 | 16.7 | 12.4 | 17.2 | 7.8 | 19.6 | 12.6 | 2.3 | 18.2 | 15.6 |

**Abbreviations for parameters are: TPH (total petroleum hydrocarbons), 2MNa (2-Methylnaphthalene), ACE (Acenaphthene), ACY (Acenaphthylene), AN (Anthracene), BaA (Benzo(a)anthracene), BaP (Benzo(a)pyrene), CH (Chrysene), DA (Dibenz(a,h)anthracene), FLU (Fluoranthene), FL (Fluorene), NA (Naphthalene), PH (Phenanthrene) and PY (Pyrene).*

**Table B4** Relative frequency of exceedances (%) of metals and polychlorinated biphenyls (PCBs) per SCH.

| SCH | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn | Total PCBs |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0 | 0.0 | 0.0 | 16.7 | 8.3 | 0.0 | 75 | 41.7 | 0.0 |
| 2 | 0.0 | 0.0 | 0.0 | 10.7 | 0.0 | 0.0 | 3.6 | 0.0 | 7.1 |
| 3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 0.0 | 0.0 | 0.0 | 4.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.3 | 0.0 |
| 8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.9 | 0.0 | 7.1 |
| 9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 10 | 0.0 | 0.0 | 0.0 | 20 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 11 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4 | 0.0 | 0.0 |
| 12 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 13 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 14 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 |
| 15 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 16 | 0.0 | 0.0 | 0.0 | 11.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 17 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 18 | 0.0 | 0.0 | 4.6 | 4.6 | 0.0 | 22.7 | 9.1 | 9.1 | 0.0 |
| 19 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 20 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 16.7 | 0.0 | 0.0 |
| 21 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0 | 0.0 | 0.0 |
| 22 | 0.0 | 0.0 | 0.0 | 7.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 23 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 24 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 25 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.3 | 0.0 |
| 26 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 27 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 28 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 29 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 30 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 31 | 5.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| mean | 0.18 | 0.00 | 0.15 | 2.42 | 0.27 | 0.73 | 3.62 | 1.92 | 0.62 |

# APPENDIX C Copyright Agreement Letters for Co-Authorship

March 02, 2022

Dr. Tony R. Walker
School for Resource and Environmental Studies
Dalhousie University
Halifax, NS
B3H 4R2

I am preparing my Master of Environmental Studies (MES) thesis for submission to the Faculty of Graduate Studies at Dalhousie University, Halifax, Nova Scotia, Canada. I am seeking your permission to include a manuscript version of the following paper(s) as a chapter in the thesis:

**Spatiotemporal characterization of petroleum hydrocarbons and polychlorinated biphenyls in small craft harbour sediments in Nova Scotia, Canada**
Myriam Mora, Tony R. Walker, Rob Willis
Marine Pollution Bulletin, Accepted, 2022

**Multiple contaminant ecological risk evaluation in small craft harbour sediments in Nova Scotia, Canada**
Myriam Mora, Tony R. Walker, Rob Willis

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Full publication details and a copy of this permission letter will be included in the thesis.

Yours sincerely,

Myriam Mora [redacted]

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Name: Tony R. Walker Title: Associate Professor

Signature: [redacted] Date: March 2, 2022

March 03, 2022

Mr. Rob Willis
Dillon Consulting Limited
Halifax, NS
B3S 1B3

I am preparing my Master of Environmental Studies (MES) thesis for submission to the Faculty of Graduate Studies at Dalhousie University, Halifax, Nova Scotia, Canada. I am seeking your permission to include a manuscript version of the following paper(s) as a chapter in the thesis:

**Spatiotemporal characterization of petroleum hydrocarbons and polychlorinated biphenyls in small craft harbour sediments in Nova Scotia, Canada**
Myriam Mora, Tony R. Walker, Rob Willis
Marine Pollution Bulletin, Accepted, 2022

**Multiple contaminant ecological risk evaluation in small craft harbour sediments in Nova Scotia, Canada**
Myriam Mora, Tony R. Walker, Rob Willis

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Myriam Mora [redacted]

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Name: Rob Willis Title: Senior Toxicologist/Risk Assessor; Adjunct Professor

Signature: [redacted] Date: March 25th, 2022