SPATIO-TEMPORAL POLYCYCLIC AROMATIC HYDROCARBON (PAH) CHARACTERIZATION AND ASSESSMENT IN SMALL CRAFT HARBOUR SEDIMENTS IN NOVA SCOTIA

by

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Submitted in partial fulfilment of the requirements
for the degree of Master of Environmental Studies

at

Dalhousie University
Halifax, Nova Scotia
November 2018

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Small craft harbour (SCH) environments play an important role in the fisheries industry of Nova Scotia (NS). SCHs support various fisheries and are federally managed by Fisheries and Oceans Canada (Small Craft Harbours), in support of this sector. SCHs, similar to other coastal environments, are prone to point and non-point sources of contamination which can pose a risk to biota and human health. This study examines one common class of contaminants which find their way into harbour sediments: polycyclic aromatic hydrocarbons (PAHs). In a multi-faceted approach, PAHs were evaluated across 31 SCHs in NS for the temporal period of 2001-2017, with improved characterization and source apportionment of PAHs as two key research objectives. Results indicate that the majority of SCHs across NS demonstrate PAH concentrations best characterized as low risk to biota (based on empirical sediment quality guidelines) and are dominated by compounds which have low mobility in the water column. Multiple lines of evidence indicate that PAHs in NS SCHs are mainly produced by combustion processes, including coal combustion, biomass combustion, and vehicular emissions. Furthermore, the implemented research approaches and recommendations of this study demonstrate usefulness and support for federal SCH management across Canada.

LIST OF ABBREVIATIONS USED

1-MN	1-Methylnaphthalene
2-MN	2-Methylnaphthalene
Ace	Acenaphthene
Acy	Acenaphthylene
Ant	Anthracene
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BghiP	Benzo(g,h,i)perylene
BkF	Benzo(k)fluoranthene
CCME	Canadian Council of Ministers of the Environment
Chr	Chrysene
DFO	Fisheries and Oceans Canada
DBahA	Dibenz(a,h)anthracene
ERL	Effects Range Low
ERM	Effects Range Median
Flu	Fluoranthene
Fl	Fluorene
HMW	High Molecular Weight
IP	Indeno(1,2,3-cd)pyrene
ISQG	Interim Sediment Quality Guideline
LMW	Low Molecular Weight
Nap	Naphthalene
NOAA	National Oceanic and Atmospheric Administration
NS	Nova Scotia
Pery	Perylene
Phe	Phenanthrene
PAH	Polycyclic Aromatic Hydrocarbon
PEL	Probable Effect Level
Pyr	Pyrene
SQG	Sediment Quality Guideline
SCH	Small Craft Harbour
US EPA	United States Environmental Protection Agency

ACKNOWLEDGEMENTS

This thesis would not be possible without the support of my supervisor, Dr. Tony R. Walker. Thank you for allowing me to think critically and freely, while consistently supporting my ideas for this research. I feel very lucky to have had a supervisor who has been so invested and engaged with my work and demonstrated confidence in my abilities. Your support of students in SRES is unparalleled and I feel extremely fortunate to have worked with you. I would also like to thank my committee members Rob Willis and Dr. Michelle Adams for all of their guidance and encouragement. This research experience has been extremely rewarding thanks to each of you.

I am incredibly grateful to Fisheries and Oceans Canada Small Craft Harbours (DFO-SCH) and Public Services and Procurement Canada (PSPC) for their support in providing historical sediment data and enabling this research to come to life. Special thanks to Tamara McFarland, Troy Young, and John Appleby for their time and efforts.

Thank you to Dr. Gary Norris and Dr. Ronald Henry for supporting the application of Unmix Optimum as part of this research. Without the both of you, this part of the thesis would not have been possible. I am very grateful for all of the advice and support you both have provided to me.

Thank you to Professor Raymond Côté for acting as external examiner for my defence.

I would to acknowledge Dalhousie University and the Province of Nova Scotia for generous funding through the SRES Legacy Scholarship and the Nova Scotia Graduate Scholarship that has made this research possible. Similarly, this work was supported by NSERC Discovery Grant RGPIN-2018-04119 to T.R.W.

Last, and certainly not least, thank you to my Mom and Dad for their ongoing encouragement and support of my pursuits.

CHAPTER 1 INTRODUCTION

1.1 SEDIMENT CONTAMINATION IN MARINE HARBOURS: AN ENVIRONMENTAL ISSUE

Marine harbour environments, characterized by their location along ocean water bodies, represent sites which serve social, historical, and economic purposes (Walker et al., 2015a; Walker, 2016). Regardless of size or purpose, marine harbours are prone to contamination inputs to water and sediment from a variety of sources, often influenced by anthropogenic activities, including activities specifically associated with harbour operation and use (Walker, 2016). Inputs to harbour environments can include organic compounds (e.g., polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], inorganic compounds [metals], biological components [bacteria/sewage], and material items including plastics and littered debris (Walker et al., 2013a; Walker, 2016). Contaminants enter harbours by point and non-point sources, including industrial and residential sources and by direct spills, which may contribute to harbours from upstream activities (Burton et al., 2001; Lima et al., 2005). Contamination varies in extent, and can depend on many different factors, including physicochemical characteristics of harbour sediment, harbour location, harbour use, and contamination sources (Ke et al., 2005; Chen et al., 2012; Walker et al., 2013b).

1.1.2 Importance of Sediment Quality in Marine Harbours

Sediments tend to accumulate and gather contaminants, especially those which are hydrophobic, as these contaminants tend to sorb easily to particulate matter and settle into sediment (Tolosa et al., 2004; Manariotis et al., 2011). Marine sediment quality in harbours is of great ecological importance (Kwok et al., 2013). For example, sediment plays a key role in aquatic food webs and support various biological and chemical cycles (Burton et al., 2001). Similarly, sediment is home to many benthic organisms, including clams, lobsters, and sponges, which feed and live along the ocean floor. Contaminated sediment can negatively impact biota which live within or around sediment and can further hinder pelagic species at various depth levels of the water column if contaminants remain suspended or become re-suspended (Mearns et al., 2010; Chapman and Mann, 1999). Sediment quality is of concern for environmental managers as sediment can behave as both a source and/or a sink for contaminants (Chapman and Mann, 1999; Ahlf et al., 2002; Hwang et al., 2013; Franz et al., 2014). Sediment contamination is considered an environmental issue and has been recognized by scholars for decades (Larsson, 1985; Hong et al., 1995; Lima et al., 2005). This issue extends beyond academic studies into the realm of control and management of hydrophobic contaminants in sediments which may strongly sorb and persist for long periods, making management complex (Luthy, 2004; Tolosa et al., 2004). Sediment management practices vary among sites and can include processes such as sediment dredging, remedial processes, and reclamation activities.

1.2 CONTAMINANTS OF POTENTIAL CONCERN: POLYCYCLIC AROMATIC HYDROCARBONS

PAHs are organic contaminants that are extremely ubiquitous in marine sediments of harbours of the world (Lima et al., 2005; Stout et al., 2015). Due to their chemical structure and hydrophobicity, PAHs can accumulate and persist in sediments over time, making them difficult to manage (Jiao et al., 2009; Wu et al., 2014; Li et al., 2015). The global presence of PAHs in harbour sediments is supported by the fact that PAHs can be produced from many sources, including combustion (pyrogenic) processes, petrogenic inputs, and by natural processes (Yunker et al., 2002; Stout et al., 2015; Masood et al., 2016). PAH sources that are anthropogenic in nature are considered the most impactful of all sources, which encompasses processes including coal combustion, industrial waste, and oil spills (Lima et al., 2005; Mostert et al., 2010; Stout and Graan, 2010). PAHs are considered contaminants of concern in many jurisdictions given their ecological and human health impacts (Stout et al., 2015). PAHs may present risks to aquatic biota in harbour environments, as they can be toxic and can bioaccumulate in tissue (Thorsen et al., 2004; Kupryianchyk et al., 2012). PAHs may also present human health concerns. For example, certain PAHs have carcinogenic properties, and there is potential risk to humans who ingest PAH-affected aquatic biota (Jiang et al., 2009; Fang et al., 2012; US EPA, 2014).

The persistence of PAHs, their risk to aquatic and human health, accompanied by the many sources in which they can originate, makes them a class of contaminants which can be difficult to manage in harbour sediment. The ubiquity of PAHs has extended into many large Canadian harbours including Vancouver Harbour (BC), Halifax Harbour (NS), and Saint John Harbour (NB), (Tay et al., 1992; Zitko, 1999; Bolton et al., 2004), and similarly presents challenges and risks to Canadian small craft harbours (SCHs).

1.3 CANADIAN MARINE HARBOURS: SMALL CRAFT HARBOURS

In Canada, marine harbours play a large role in supporting the economy by contributing to the fishery industry as valuable infrastructure (DFO, 2018a). The majority of marine harbour environments in Canada are classified as SCHs, which represent small water lots that serve fishing or recreational purposes, under the national mandate of Fisheries and Oceans Canada Small Craft Harbours program (DFO-SCH) (DFO, 2018a). The DFO-SCH program manages 1008 SCHs across Canada, with 882 (87.5%) designated as fishing harbours, while 126 (12.5%) serve recreational purposes (DFO, 2018a). The national collective value of the infrastructure of the DFO-SCH program is approximately $5.6 billion CAD (DFO, 2018a). Atlantic Canada, formed by the provinces of Nova Scotia (NS), New Brunswick (NB), Prince Edward Island (PE), and Newfoundland and Labrador (NL), is particularly abundant in SCHs, with 639 included as part of the SCH program (DFO, 2018a). The abundance of SCHs in the Atlantic region directly supports various fisheries, making Atlantic Canada responsible for the largest volume of landings for commercial sea and freshwater fisheries in Canada (DFO, 2018b). SCHs play a significant role in the fishery industry nationwide, further solidifying their economic and cultural importance in the Canadian marine landscape.

1.3.1 Nova Scotia SCHs and PAHs

The province of Nova Scotia is home to 178 SCHs, the majority of which are core fishing harbours. These SCHs are extremely important because NS has the greatest live weight landings (and value) for total commercial sea fisheries provincially in Canada (DFO, 2018b). The largest sea fisheries in NS on a live weight basis (as of 2016) are lobster, herring, and scallops (DFO, 2018b). SCHs in NS, which directly support the various fisheries above, reside along three major water bodies: Gulf of Saint Lawrence, Atlantic

Ocean, and the Bay of Fundy. NS SCHs, similar to other harbours of the world, are not exempt from sediment contamination by PAHs (and other contaminants) and are subsequently assessed for sediment quality routinely by DFO-SCH. This approach supports the notion that sediment quality management is an important consideration to ensuring SCHs are productive and healthy environments for years to come. The sampling of individual SCHs by DFO-SCH across NS (and among other provinces) has led to an enormous amount of sediment data that has helped identify commonalities and trends. As such, one trend, supported by review of historical sediment assessments and supplemented by discussion with NS SCH managers, is the indication that PAHs are ubiquitous in NS SCHs and are concerning to SCH managers (Walker et al., 2013a).

1.4 PROJECT BACKGROUND AND APPROACH

The complexity and ubiquity of PAHs in sediments, coupled with the importance of sediment quality in NS SCHs, are the two key principles at the core of this research. To accompany these principles, this research focuses on three concepts specific to PAHs in NS SCH sediment: (i) assessment; (ii) source characterization; and (iii) management. To date, a comprehensive multi-harbour spatiotemporal assessment of PAHs in sediment of NS SCHs has yet to be completed. Therefore, this research specifically explores the assessment and source characterization of PAHs in NS SCH sediments in support of environmental management of these sites. To accomplish this, historical sediment data was acquired from DFO-SCH for 31 SCHs across NS for the period of 2001-2017.

1.4.1 Assessment of PAHs in NS SCHs

Assessment of PAHs in NS SCH sediments is completed by sediment sampling by DFO-SCH. DFO-SCH routinely assesses sediment as part of their Marine Sediment Sampling Program (MSSP). MSSPs are conducted on an individual harbour basis and have produced a large volume of sediment data over time. Data gathered from MSSPs is presented in a federal report format, which is not publicly available. However, sediment quality data for NS SCHs has yet to be assessed or analyzed beyond harbour-specific assessments of the MSSP. As NS SCH managers have identified PAHs as contaminants of potential concern and are very aware of their presence in NS SCH sediment, this has offered an opportunity to work with MSSP data in a comprehensive multi-harbour spatiotemporal approach. By holistically reviewing temporal (2001-2017) sediment data from 31 SCHs, the distribution of PAHs can be further assessed at the harbour level, and within the DFO management regions of the province (Gulf, Eastern, Southwest). This approach provides insight to which harbours and/or regions of the province require the most attention and may contribute to the prioritization of federal government spending for SCHs.

1.4.2 Source characterization of PAHs in NS SCHs

Source characterization and source control of contaminants are two important considerations of managing federal sites in Canada and are concepts which are inter-connected (FCSAP, 2017). Simply put, if you are able to characterize contamination sources, source control efforts are likely to be more impactful and successful. As SCHs are federally managed sites, these two considerations are very important in regard to federal environmental liabilities associated with understanding potential sources of contaminants and environmental management approaches. PAH sources, specifically, can be difficult to characterize, control, and subsequently manage as they can occur from many sources of both anthropogenic and natural origins (Tobiszewski and Namieśnik, 2012).

Source apportionment approaches, which aim to characterize possible sources, can estimate PAH sources by using previously collected data. However, source apportionment for PAHs (and other contaminants) is not currently included as part of the MSSP. Despite this, the spatiotemporal DFO-SCH MSSP dataset has information specific to individual PAH compounds for each sediment sample gathered, which proves extremely useful for source apportionment methods. This dataset presented an opportunity to examine source apportionment of PAHs at harbour, regional, and provincial scales. Application of source apportionment approaches can result in a better understanding of PAH sources, which is invaluable for SCH managers, as source control efforts can then be better explored. More specifically, source apportionment of PAHs assists SCH managers by providing them with insight to pro-actively manage (via adaptive management) and better understand historical, current, and future PAH inputs to SCHs.

1.5 RESEARCH OBJECTIVES

The three objectives of this research are:

1. Characterize the distribution of PAHs in NS SCHs at the individual harbour level and across the Gulf, Eastern, and Southwest regions of NS
2. Assess source apportionment of PAHs across NS SCHs by employing multiple lines of evidence, including PAH diagnostic ratios, US EPA Unmix Optimum receptor modelling, and PAH compositional analysis
3. Employ objectives 1 and 2 to form evidence-based recommendations to support SCH management in NS and beyond, particularly in terms of prioritizing SCHs and efficient use of federal government spending.

1.6 THESIS ORGANIZATION

This thesis is organized into six (6) chapters. Following this introductory chapter (Chapter 1), Chapter 2 is a review of relevant literature and background information pertinent to this research. Chapter 3 discusses the methodological approaches used. Chapters 4 and 5 are presented as stand-alone journal articles with their own abstracts, introductions, methods, results, discussions, conclusions, and references. Chapter 4 focuses on improved assessment and characterization of PAHs across NS SCHs and was prepared for and successfully published in the journal Marine Pollution Bulletin. Chapter 5 is focused on source apportionment of PAHs in NS SCHs and was prepared for submission to the journal Science of the Total Environment. As chapters 4 and 5 are stand-alone articles, concepts included in these chapters may be similar in nature to topics covered in earlier chapters. Repetition of certain concepts can be expected. Chapter 6 explores management implications and recommendations derived from the findings presented in Chapters 4 and 5, alongside a summarized discussion and concluding remarks that expand across all chapters and reflects on the over-arching principles of the study.

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CHAPTER 2 BACKGROUND

2.1 SMALL CRAFT HARBOURS

Canadian small craft harbours (SCHs) are characterized by a small size and placement along rural coastal communities (Walker et al., 2013a). The national DFO-SCH program focuses primarily on core fishing SCHs by encouraging local control and involvement for non-core fishing harbours through the establishment of Harbour Authorities (formed from members of the local community), while making the divestiture of less active SCHs (e.g. recreational harbours) a priority (DFO, 2016). As part of their management objectives, DFO-SCH aims to ensure SCHs are accessible, safe, operational, and in good condition (DFO, 2018a).

NS SCHs (alongside those in NB and PE) are included as part of the Maritimes and Gulf Region of the national DFO-SCH program. Furthermore, DFO-SCH has organized NS SCHs into three provincial management regions: Gulf, Eastern, and Southwest (DFO, 2013). The Gulf region defines SCHs from the NB-NS border to the upper western tip of Cape Breton Island. SCHs in the Gulf region support inshore fisheries (fisheries that occur in water depths up to 30 meters) and are closed during the winter months due to ice cover. The Eastern region resides from the eastern tip of Cape Breton Island and down the North Atlantic coast, including Cumberland and Colchester counties. SCHs in this region mainly support inshore fishing and are small in size. SCHs that reside along the Bay of Fundy are open in the winter months, while those residing on the Atlantic side are closed due to ice. The Southwest region defines SCHs in the southern portion of the province, encompassing harbours along both the Atlantic Ocean and the Bay of Fundy. SCHs in this region are open year-round and support various fisheries including lobster, ground fish, and herring (DFO, 2013). The NS SCH management regions are presented in Figure 2.1.

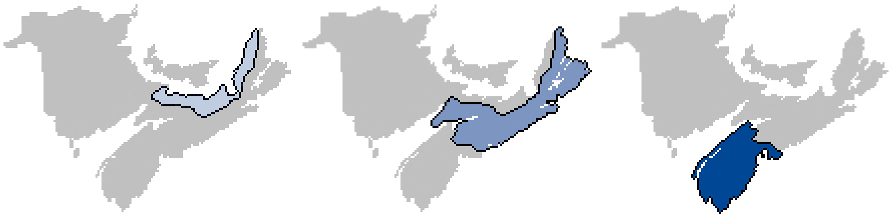

Figure 2.1 Gulf, Eastern, and Southwest (left to right) DFO-SCH management regions of NS SCHs, adapted from DFO (2013).

2.2 SCH MANAGEMENT: MARINE SEDIMENT SAMPLING PROGRAM (MSSP)

In fulfillment of DFO-SCH management objectives, sediment assessments are regularly completed. To ensure SCHs are accessible and operational, sediment assessments are routinely completed prior to dredging activities. Dredging is the process by which sediment is removed from the harbour to ensure that vessels can navigate the channel. Prior to dredging, a marine sediment sampling program (MSSP) is completed to provide sediment quality information that is used to determine dredged sediment disposal options. MSSPs are in place to inform harbour decision makers of potential sediment contamination in SCHs (Walker et al., 2013a). The MSSP is an environmental management tool that focuses on the immediate (current) contamination levels of harbour sediment and is primarily focused on informing disposal options (Walker et al., 2013a). To do so, sediment samples are collected and analyzed, and the analytical results are then compared to various environmental quality guidelines, including those developed by the Canadian Council of Ministers of the Environment (CCME). Federal SCH managers are tasked with determining disposal options for sediment by the extent of contamination and which contaminants are present, as presented in MSSP reports. Disposal options for sediment include (but are not limited to): disposal at sea, on-land containment cells, landfills, confined storage, and use for beach nourishment. Sediments which are heavily contaminated and exceed multiple environmental quality guidelines require more intensive and subsequently expensive disposal options, which may include soil/sediment treatment processes that may require increased transportation of dredged material (Walker et al., 2013a).

Federal managers of SCHs determine viable sediment disposal options through comparison of sediment analytical data to environmental quality guidelines (Walker et al., 2013a). Specifically, samples are compared to Canadian Environmental Quality Guidelines (CEQGs). For example, to assess at sea sediment disposal options, the *Canadian Environmental Protection Act* (CEPA, 1999) Disposal at Sea Regulation Guidelines are used as the point of reference. Assessment of land-based sediment disposal options may rely on guidelines including CCME Soil Quality Guidelines, CCME Sediment Quality Guidelines (SQGs), CCME Water Quality Guidelines (WQGs), Atlantic Risk-Based Corrective Action (RBCA) Risk-Based Screening Levels (RBSLs) and Sediment Ecological Screening Levels (SESLs), Health Canada Guidelines for Drinking Water Quality (CGDWQ), and province-specific guidelines for landfill disposal. Leachate studies may be completed as part of MSSPs to help support disposal decisions. Leachate studies often address on-land disposal options and are completed to determine the likelihood of certain sediment contaminants entering potable water sources by vertical migration through soil to groundwater (Walker et al., 2013a).

2.2.1 MSSP Sediment Sampling Design

The specific approaches of the MSSP are governed by Terms of Reference (TOR) created by the federal government (Appendix A). As per MSSP TOR, sediment sampling is to be completed by using a grid format (PSPC, 2014). A grid is applied to the proposed dredging area in the SCH and each box within the grid is assigned a number. Grids must include a minimum of thirty cells and a random number generator selects boxes within the grid to determine where sediment sampling is to occur. The number of sediment samples depends primarily on the dredging area and volume of sediment which is to be dredged (Environment Canada, 1994; PSPC, 2014). Samples are most commonly grab samples which gather surficial sediment between 0-10 cm in depth (Walker et al., 2013a). Sediment sampling in the MSSP program is completed as per Environment Canada's *Guidance Document on Collection and Preparation of Sediments for Physicochemical*

Characterization and Biological Testing (1994). This document highlights that in most cases, 1-5 sediment samples can be used to assess sediment quality (Environment Canada, 1994).

2.3 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

PAH compounds are persistent organic contaminants that are formed from aromatic rings (a minimum of two) made from carbon and hydrogen (McCready et al., 2000; Collier et al., 2013). PAHs are probable carcinogens, demonstrate various other toxic effects, and can impair biota (Thorsen, 2004; Kupryianchyk et al., 2012; Stout et al., 2015). Given these characteristics, both the United States Environmental Protection Agency (US EPA) and many other nations list PAHs as priority pollutants (Tobiszewski and Namieśnik, 2012; US EPA 2014; Stout et al., 2015). The US EPA lists the following 16 PAHs as priority pollutants: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd) pyrene. The 16 priority PAHs represent “parent” or “unsubstituted” PAHs, indicating they do not have an attached alkyl group (Zemo, 2009). Alkyl groups are the addition of carbon and hydrogen atoms to the atomic rings of the PAH. Many other PAHs exist, of which are alkylated and derived from the parent PAH compound (substituted PAHs) (Stout et al., 2015). However, given the cost of analytical testing and the known toxicity of the US EPA priority PAHs, these 16 PAHs are most commonly tested and assessed as part of environmental management approaches (Zemo, 2009; Stout et al., 2015). A comparison of unsubstituted and substituted PAHs is presented in Figure 2.2.

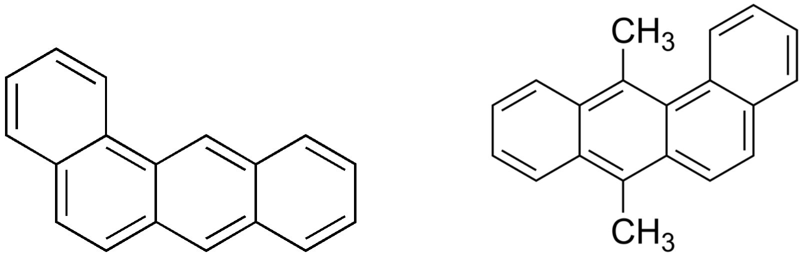

Figure 2.2 Comparison of unsubstituted benzo(a)anthracene, a US EPA priority PAH (left) and 7,12-dimethylbenzo(a)anthracene, a substituted PAH (right). The two methyl groups (CH_3) in the substituted PAH represent two attached alkyl groups.

Defining characteristics of PAHs include the number of atomic rings they contain, their molecular weight (g/mol), and their classification as either low or high molecular weight. PAHs contain between 2 and 6 atomic rings and the number of rings a PAH contains influences the molecular weight of the compound, such that more atomic rings increase the molecular weight (Hwang et al., 2003; Mostert et al., 2010). PAHs that possess 3 or less atomic rings are defined as low molecular weight (LMW), while PAHs that possess 4 (or more) atomic rings are defined as high molecular weight (HMW) (CCME, 2010). For example, benzo(a)anthracene is best described as an HMW PAH with four rings and a molecular weight of 228 g/mol.

2.3.1 PAHs in Atmospheric and Aquatic Environments

PAH compounds that are emitted into the atmosphere are either in gaseous phase or adhered to particulate matter (PM), also known as particulate phase (Tobiszewski and Namieśnik, 2012). Whether PAHs will be in the gas or particulate phase depends on such factors as: the size of the released PAH compounds (molecular weight), the organic and inorganic carbon content of atmospheric particles, the atmospheric temperature, and the amount of PM present in the atmosphere. It is assumed that lighter PAH compounds (LMW) will be present in the gas phase, while heavier PAH compounds (HMW) are more likely to adhere to particulate matter (Neff, 2005; Tobiszewski and Namieśnik, 2012). PAHs can change phases in the atmospheric environment, with some PAHs being emitted as gases, but which can subsequently adhere to PM under certain conditions (Marr et al., 2006).

PAHs that adhere to PM (particle phase PAHs) in the atmosphere are thought to better maintain their integrity in the environment because of the protection PM particles provide (Yunker et al., 2002). Similarly, if PAH compounds sorb to larger sized PM in the air, or are completely engulfed within PM, they will have a greater likelihood of integrity as they move through the environment (e.g., emission source to sediment) (Yunker et al., 2002). The protective features that PM may provide (which may rely on PM chemistry and sorption characteristics) can play a role in how PAH compounds are influenced by environmental fate processes, including their interaction with other compounds in the atmosphere and different chemical processes, including photolysis and photooxidation (Marr et al., 2006).

The behavior of PAHs in the atmospheric environment is often directly related to PAHs in the aquatic environment because PAHs which enter aquatic environments often underwent emission to air and transport in the atmosphere before deposition into water bodies. PAHs find their way into harbour sediment by deposition of atmospheric emissions onto water surfaces, or by direct inputs into harbours by spills/dumping or infrastructural inputs (e.g., PAHs entering harbours by creosote treated timbers) (Tobiszewski and Namieśnik, 2012; Stout and Graan, 2010). In aquatic environments, LMW PAH compounds are more water soluble than high molecular weight HMW PAHs. Given the increased solubility of LMW PAHs, these PAHs are more likely to be present in the upper water column of aquatic environments, while HMW PAHs are more likely to accumulate and remain in sediment. The characteristics of PAHs, alongside physicochemical characteristics of sediment, can impact the bioavailability of PAHs to biota and influence the behavior of PAHs in aquatic environments.

2.3.2 The Relationship Between PAHs And Sediment Physicochemical Characteristics

Physicochemical characteristics of sediments including grain size, organic matter, and carbon content are important considerations in best understanding PAH fate and behavior in harbour environments (Tsapakis et al., 2003; Ghosh and Hawthorne, 2010). The ability of sediment to retain PAHs can be influenced by grain size and organic matter content (Viguri et al., 2002; Ghosh and Hawthorne, 2010). In general, sediments with a smaller grain size, characterized by a greater percentage of silt and clay, tend to be more heavily contaminated because of their increased surface sorption capacity (Pourabadehei and Mulligan, 2016). The organic matter content of sediment can specifically influence the accumulation of PAHs, as PAHs can bind to the carbon present within the organic matter of the sediment (Koelmans et al., 2006). The carbonaceous structures in sediment are rigid, HMW aromatic structures, and their physical structures contribute to their ability to sorb PAHs (and reduce the inherent bioavailability of PAHs in the process) (Achten and Hoffmann, 2009). There are many different carbon sources in sediments, including soot carbon, coal particles, and kerogen, all of which behave differently in their binding and releasing ability of PAHs (Cornelissen et al., 2006). Similarly, carbon can be introduced to sediments by natural organic matter in aquatic environments (plants, wastes) or by inputs from sewage.

Despite the general understanding of the link between carbon and PAHs in aquatic environments, the relationship between total organic carbon content (TOC) of sediment and PAHs is one which is not unified within the literature. Scholars have discussed the relationship between PAHs and TOC in sediments of harbour environments and the findings demonstrate the relationship to be positive, negative, or lacking altogether. Similarly, scholars have suggested that TOC and PAHs could simply both be emitted into marine environments and that the relationship between TOC and PAHs may not always be direct (Liu et al., 2013a).

2.4 PAH SOURCES

In the environment, PAHs are released as mixtures, containing multiple PAH compounds (CCME, 2010; Tobiszewski and Namieśnik, 2012). PAHs are generated by various processes and originate from sources often organized into the following groups: pyrogenic, petrogenic, or biogenic/natural. Pyrogenic PAHs are created as a result of fossil fuel and organic matter combustion processes, which emit PAHs directly into the air (Masood et al., 2016). Pyrogenic sources of PAHs are associated with combustion processes and can include PAHs which are formed by the intentional process of pyrolysis (EPRI, 2008). In contrast, petrogenic sources of PAHs originate from petroleum (crude and refined) (da Silva and Bicego, 2010; Masood et al., 2016).

Pyrogenic PAH sources are more difficult to define due to their discharge into the atmosphere and later deposition into aquatic environments (Stout and Graan, 2010; Tobiszewski and Namieśnik, 2012). PAH compounds can occur naturally in the environment from processes including the formation of rock from sediment (diagenesis) and forest fires Mahanty et al., 2011). Studies have indicated that some PAH compounds (naphthalene, phenanthrene, and perylene) can be produced both biologically and by anthropogenic activities (Mahanty et al., 2011). The molecular weight of PAHs produced by different emission sources can differ, as low temperature combustion tends to yield LMW PAHs, while high temperature combustion yields HMW PAHs (Mosert et al., 2010). Higher weight PAH compounds occur from the burning of oil, coal, forest fires, or biomass burning, may remain in environments for longer periods (persist), and are more toxic (Smith et al., 2009; Evans et al., 2016).

2.5 FORENSIC ASSESSMENT OF PAHS

As PAHs from different emission sources can differ in their environmental impacts, forensic assessment of PAHs is needed to understand ecological and human health impacts (Tobiszewski and Namieśnik, 2012). Forensic assessment of PAHs has been explored over the last fifty years. Early forensic assessments of PAHs in the 1970's carefully examined PAH characteristics (such as levels of alkylation) to help provide insight to potential emission sources (Wise et al., 2015; Stout et al., 2015). Over time, as technology and the understanding of PAHs and their emission sources improved, forensic assessment methods have continued to advance (Lima et al., 2005; Walker et al., 2017; Nádudvari et al., 2018).

2.5.1 PAH Diagnostic Ratios

PAH diagnostic ratios are a very popular approach to forensically assessing PAHs and are particularly useful in differentiating between pyrogenic and petrogenic PAH sources. However, diagnostic ratios are not always absolute and should be used with discretion as inter-source similarities can weaken PAH source estimations (Galarneau, 2008). Despite this, many PAH diagnostic ratios have been applied in the literature and have been accompanied by transitional values that help to distinguish between sources (Budzinski et al., 1997; Dickhut et al., 2000; Yunker et al., 2002; Fang et al., 2003; Tobiszewski and Namieśnik, 2012).

PAH alkylation (the presence of alkyl groups) was the starting point at which scientists started to better understand the sourcing of PAH compounds, and eventually led to the use of PAH diagnostic ratios (Stout et al., 2015). Scientists began to discover that the way in which PAH compounds were produced (high/low heat processes, and either produced rapidly or over a long period) revealed different proportions of PAH compounds (Stout et al., 2015). These findings formed the scientific foundation for PAH diagnostic ratios, in that PAHs, similar in their physicochemical properties, such as molecular weight, aqueous stability, and octanol-water partition coefficient (K_{ow}), will retain their relative concentrations in the environment over time, despite weathering or other natural environmental influences (Costa and Sauer Jr, 2005; Zemo, 2009). Since PAH ratios can maintain their relative proportions in the environment, they can provide insight into the specific source from which they came. Ultimately, PAH isomers (compounds with identical chemical composition, yet different orientation) that have similar properties will not demonstrate vast differences in their environmental movement as they have a high likelihood to degrade or be influenced by environmental factors at similar rates (Zemo, 2009).

Diagnostic ratios estimate PAH sources by examining the difference between two PAHs in an isomeric pairing, which is formed by one “kinetic” and one “thermodynamic” PAH. PAHs which demonstrate a lower stability are referred to as kinetic, while those which are more stable are considered thermodynamic (Yunker and Macdonald, 1995). As an example, this is reflected in the commonly used PAH ratio of anthracene/(anthracene+phenanthrene) (Ant/Ant+Phe), in which anthracene is the more kinetic PAH in comparison to thermodynamic phenanthrene (Yunker et al., 1996). Ratio transition values have been defined by many scholars in the literature, including Yunker et al. (2002), Dickhut et al. (2000), Budzinski et al. (1997). For this specific ratio, Budzinski et al. (1997) have defined transitional values to aid in its interpretation. Specifically, if the ratio is <0.10, it suggests petrogenic sourcing, while a ratio >0.10 suggests pyrogenic (combustion) sources. A low ratio reveals a greater amount of phenanthrene, while a higher ratio reveals a greater amount of anthracene, which proves useful in estimating whether PAHs originate from petrogenic or pyrogenic sources.

2.5.2 Multivariate Receptor Modelling

Multivariate receptor models (MRMs) are widely used for environmental research purposes, commonly in the monitoring of contaminants (Henry and Christensen, 2010). In the 1960s, when receptor modelling began to grow, approaches were very much focused on atmospheric (air quality) data, but MRMs have since evolved and are commonly used for evaluating other forms of environmental data, including data derived from sediment (Hopke and Cohen, 2011). Popular multivariate receptor models include chemical mass balance models (CMB), positive matrix factorization (PMF), and Unmix, all of which are considered advanced receptor models (Song et al., 2008). CMB, PMF, and Unmix are commonly employed by the US EPA, and software downloads for these models are conveniently accessible on the US EPA website (Henry and Christensen, 2010). As concern and awareness of anthropogenic contaminants, including PAHs, continues to grow, MRMs provide insight to source apportionment of contaminants and support environmental management approaches by evaluating biophysical data. MRMs focus primarily on the environment in which the pollutants reside and are less focused on the transport of the compounds from point of emission (Hopke and Cohen, 2011).

Receptor modelling tools are viewed as a complement to modelling tools that are focused on the transport and dispersal of compounds in the environment (Coulter, 2004). MRMs have three specific assumptions in their application (Henry and Christensen, 2010): *"Observed concentrations are an unknown linear sum, observed concentrations are from an unknown number of sources, and the unknown sources are of unknown composition"*.

Therefore, MRMs aim to identify the number of sources and the composition of sources (source contributions and source compositions) (Henry and Christensen, 2010). The basic mathematical model that describes the overarching goal and assumptions of multivariate receptor models is expressed in equation 1 (Henry and Christensen, 2010):

$$C=SA^T \qquad \textbf{Eq (1)}$$

- C is raw data that has been collected. C represents the known matrix of the observations (m) of species (n), and therefore is the matrix of *m x n.*
- S is the unknown matrix of source contributions, and therefore is the matrix of *m x k*, with *m* representing known observations and *k* representing the number of sources
- A is the unknown matrix of source compositions (n) of the sources (k), and therefore is represented by *n x k* matrix
- T indicates that matrix A is transposed

2.5.3 Unmix Optimum

Unmix Optimum (Unmix O) is an example of a specific MRM developed by the US EPA. Unmix was developed to compensate for various issues associated with other MRM approaches (Henry et al.,1994; Larsen and Baker, 2003). Unmix O determines how many sources best fit the data, the specific composition of the source(s), and source contributions to the data set (Henry, 2003; Lang and Yang, 2014). Factor analysis is the process by which the Unmix O model operates (Watson et al., 2008). Specifically, Unmix O looks to the data itself to determine factors (sources) which best fit (Henry, 2003;

Watson et al., 2008). To accomplish this, Unmix O uses one of two potential constrained nonlinear optimization algorithms. Unmix O does not require that sources impacting the data are previously characterized (Larsen and Baker, 2003). Unmix modelling has been previously applied to sediment data in China for forensic assessment of PAH sources (Lang and Yang, 2014) and has been applied in the Canadian Oil Sands Region to assess various contaminants (Lynam et al., 2015; Huang et al., 2016).

2.6 ASSESSING PAHs BY SEDIMENT QUALITY GUIDELINES (SQGs)

SQGs are an empirical tool used in assessment of sediment quality (Chapman and Mann, 1999; Birch, 2018). SQGs can be derived in many different ways, and often rely on biological and chemical assessments (Long et al., 1998; Chapman and Mann, 1999; Birch, 2018). SQGs are widely used as part of environmental management approaches.

In North America, commonly used SQGs are derived from the analysis of many sediment-specific studies that have been completed at various locations across North America (Long et al., 1995; MacDonald et al., 1996; Long et al., 1998). Analysis of this data has led to the development of calculated “effects range” and “effect level” SQGs (Long et al., 1995; MacDonald et al., 1996). Effects range SQGs include effects range low (ERL) and effects range median (ERM). ERL represents the concentration in which adverse effects are unlikely and is calculated by determining the 10th percentile concentration. ERM represents the concentration in which adverse effects are expected and is calculated by determining the 50th percentile concentration (Long et al., 1998). Effect level guidelines include Threshold Effect Level (TEL) and Probable Effect Level (PEL). TEL and PEL values are calculated as the geometric mean that incorporates both the 50th percentile of a dataset that demonstrates biological effects and the 85th percentile of a dataset that demonstrates no biological effects (Chapman and Mann, 1999; Birch, 2018). As ERL/ERM and TEL/PEL are calculated from a large biological effects database, they are formed on the basis of correlation. They are not derived from specific exposure and toxicity assessments and therefore do not specifically account for cause and effect (Chapman and Mann, 1999).

In Canada, CCME has developed Interim Sediment Quality Guidelines (ISQGs) and PELs for protecting aquatic life specifically in marine and freshwater systems (CCME, 2014). Canadian SQGs are strongly influenced by SQG derivation approaches that have been implemented in the United States, including the NOAA National Status and Trends Program (NSTP) (CCME, 1995). CCME ISQGs and PEL values are similar to ERL and ERM values in that ISQGs are considered lower effect level concentrations, while PEL values are higher effect level concentrations. Specific to PAHs, CCME outlines ISQG and PEL values for 13 individual PAHs: 2-Methylnaphthalene, Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Fluorene, Naphthalene, Phenanthrene, and Pyrene. Similarly, NOAA defines ERL and ERM values for the same 13 individual PAHs and ERL and ERM values for total (combined) PAHs.

SQGs have many limitations in their use (Birch, 2018). First, depending on how SQGs are derived, they can vary in their conservatism. SQGs which are overly conservative in the environment are more likely to suggest sediment toxicity when sediments do not actually pose a toxicity risk (Chapman and Mann, 1999). SQGs are also limited in that they fail to contribute information related to the bioaccumulation or biomagnification of contaminants (Chapman and Mann, 1999; Birch, 2018). SQGs are also unable to account for site specific sediment characteristics (e.g., carbon content, grain size distribution) that may play a key role in the behavior of contaminants, including mobility (Chapman and Mann, 1999). Specific to PAHs in sediments, neither CCME nor NOAA has developed SQGs for all of the 16 US EPA priority PAHs, indicating that certain PAHs do not have benchmark values. CCME has also not developed a total PAH benchmark at this time.

2.7 USE OF NON-DETECT PAH CONCENTRATION DATA

Many sediment sampling reports used in this study (MSSPs/ESAs) contain PAH concentration values which fall below the DL, indicating that the sediment PAH concentration could not be detected due to analytical instrumentation limitations. These values are presented as <DL and are considered to be “censored”. These values do not necessarily indicate that the PAH compound is not present, it simply means it is not present at a concentration high enough to be detected. It is well understood that care

should be taken in the handling of environmental non-detect data, as certain compounds can pose a risk at concentrations below a DL (Singh and Nocerino, 2002).

In assessing environmental data, non-detect data can make statistical analyses complicated and can make it difficult to calculate summary statistic values such as the mean or median (Huybrechts et al., 2002; Singh and Nocerino, 2002). As such, there are two common methods to address non-detect data: statistical methods and substitution (replacement) methods.

Statistical approaches to address non-detect data have been well defined in the literature (e.g., Dempster et al., 1977; Gleit, 1985; Gilliom and Helsel, 1986; Haas and Scheff, 1990). Statistical methods aim to address non-detect data through different estimation approaches and modelling (MacAskill, 2014). However, the utility of various statistical approaches to addressing non-detect data is limited as these methods are not commonly used by chemists and scientists in the environmental sector (Huybrechts et al., 2002). Despite this, statistical methods are more favorable as they are less-biased (Huybrechts et al., 2002) and have been found to be more robust than substitution methods in some comparison studies (Gilliom and Helsel, 1986; Haas and Scheff, 1990).

Substitution (or replacement methods) is another way to compensate for censored data. This approach simply replaces the data with another value so that it can be used in calculating values such as the mean or median for the data set. Substitution can occur by replacing the censored data with values such as a zero, ½ DL, or the DL itself. However, the substitution of ½ DL is sometimes considered more favorable than the substitution of zero or the DL itself, as these two latter approaches may result in mean and median values which are biased either too low or too high, respectively (Helsel, 1990). The ½ DL method is very popular and commonly used because it is easy to calculate and implement and it represents potential central tendency of the unknown concentration (Huybrechts et al., 2002; Singh and Nocerino, 2002). The substitution method is a recommended approach to addressing non-detects by the US EPA in their Practical Methods for Data Analysis guidance (US EPA, 2000).

In the Nova Scotia context, specific to harbour sediment, MacAskill (2014) compared a ½ DL substitution method to a robust method (statistical method) for estimating <DL values by using both PAH and other contaminant data from Sydney, Nova Scotia, and assessing the mean concentration of these contaminants. This comparison determined that the use of ½ DL generated mean values similar to those calculated by the robust statistical method for <DL data.

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CHAPTER 3 RESEARCH METHODS

3.1 ORGANIZATION OF METHODS

The methodologies of this study are best organized in a tiered approach that categorizes methods based on their support of defined research objectives and the manuscripts in which these objectives are present. Research objective one and the associated methods are detailed in Chapter 4, while research objective two and associated methods are detailed in Chapter 5. All proposed methods of objectives one and two contribute to research objective three which is discussed in Chapter 6. The proposed methodologies of this study and their alignment to specific research objectives is outlined in Table 3.1.

Table 3.1 Organization of methods used in study.

Data Acquisition	
Data Extraction	
Data Management	
Research Objective 1 [Chapter 4]: *Characterize the distribution of PAHs in NS SCHs at the individual harbour level and across the Gulf, Eastern, and Southwest regions of NS*	**Research Objective 2 [Chapter 5]:** *Assess source apportionment of PAHs across NS SCHs by employing multiple lines of evidence*
Sediment Quality Guideline Comparison for Individual PAHs	PAH Diagnostic Ratios
Aggregate PAH Calculations	Unmix O
Descriptive Statistics	PAH Profile Composition Assessment
Statistical Analysis	Statistical Analysis
Research Objective 3 [Chapter 6]: Employ objectives 1 and 2 to form evidence-based recommendations to support SCH management in NS and beyond, particularly in terms of prioritizing SCHs and efficient use of federal government spending.	

3.2 SMALL CRAFT HARBOUR (SCH) SELECTION AND STUDY AREA

A total of 31 SCHs were assessed as part of this study. The selection of these SCHs was influenced in part by a previous assessment of SCHs in NS by Walker et al. (2013a) and through consultation with federal custodians of SCHs. The name and NS DFO-SCH management region of each selected SCH is detailed in Table 3.2, while the geographical location of selected SCHs is outlined in Figure 3.1.

Table 3.2 Selected SCHs (*n*=31) and their respective DFO-SCH management region.

Gulf	Eastern	Southwest
Arisaig	Canso	Battery Point
Baileys Brook	Glace Bay	Centreville
Barrios Beach Tracadie	Neils Harbour	Clarks Harbour
Caribou Ferry	Owls Head	Delaps Cove
Inverness	Port Morien	Fox Point
Judique Baxters Cove	Three Fathom Harbour	Hampton
Pictou Landing		Hunts Point
Pleasant Bay		Little Harbour Shelburne
Skinners Cove		Little River Yarmouth
		Moose Harbour
		Pinkneys Point
		Sandford
		South Side
		Stoney Island
		Westport
		Yarmouth Bar

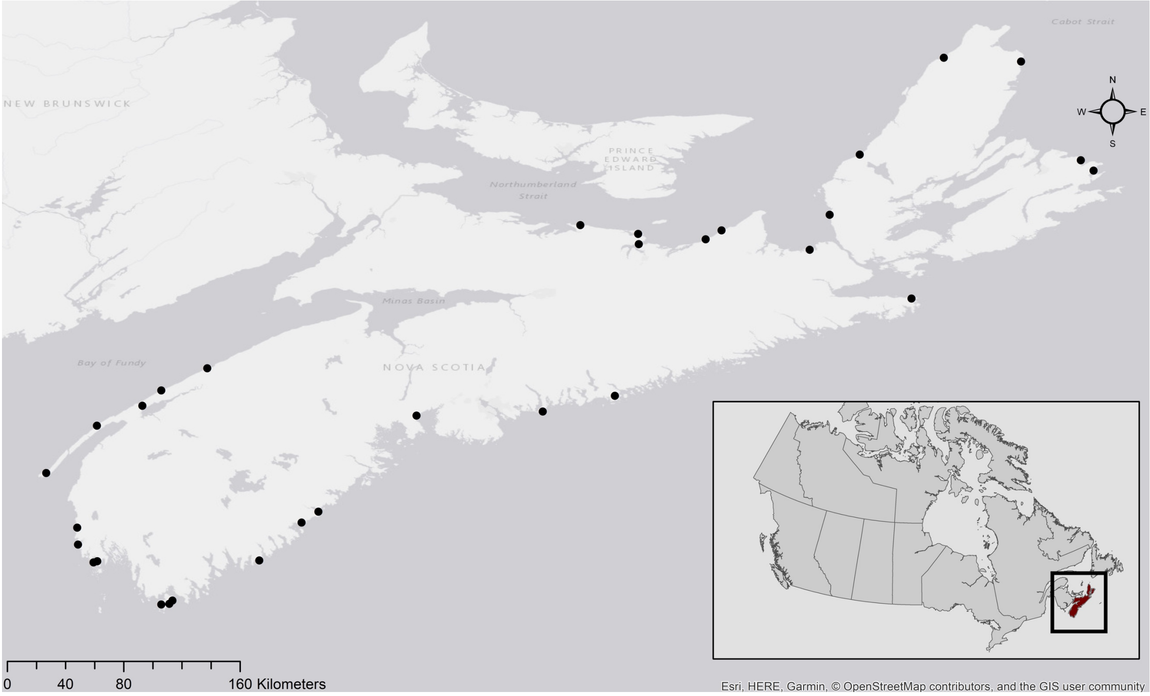

Figure 3.1 Geographical locations of selected NS SCHs.

3.3 SEDIMENT DATA ACQUISITION

To address research objectives (1-3) of this study, historical sediment data was acquired and used in all analyses. Federal SCH sediment sampling reports (*n*=115) were made available by Public Services and Procurement Canada (PSPC) on behalf of DFO-SCH, in the form of Marine Sediment Sampling Program (MSSPs) and Environmental Site Assessment (ESA) reports. Of the 115 reports, 105 were MSSP reports, while 10 were ESA reports. All sampling reports were specific to a sampling interval date, were SCH-specific (e.g., Skinners Cove, 2015), and were stored as individual electronic files. To access reports, a secure Microsoft SharePoint portal was set up by PSPC to ensure downloadable access to all files. Each report contained summarized sediment analyses specific to various contaminant concentrations, including PAHs. All reports were downloaded to an external hard drive device. The majority of reports were in portable document format (PDF), while a small number of reports were in PDF (secured) format, an indication that the report could not be modified in any way.

3.4 DATA EXTRACTION AND MANAGEMENT

To extract PAH data from reports, PDF reports (which were not secured) were exported to Microsoft Word format by Adobe Acrobat software so that the contents of the PDFs was easily transferrable. Reports which were in PDF (secured) format were kept as PDF. A Microsoft Excel file was created for each harbour with two tabs for each sampling interval (year). In the first tab, PAH concentration data in mg/kg (that was paired to sediment sample identification) was bulk copied from the Word document (PDF exports) and pasted into the Excel file. Individual PAHs included as part of this step are the following 19 compounds: 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, phenanthrene, perylene, pyrene, fluoranthene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene. The following sample-specific data was also imported: sampling date (month, day, year), analytical detection limit (DL), sample coordinates, sediment grain size distribution (% gravel, sand, silt, clay), and total carbon, total organic carbon, and total inorganic carbon concentration (g/kg). Grain size distribution and carbon specific data for the samples in these sheets was further exported and summarized regionally (Gulf, Eastern, Southwest).

3.4.1 Data Extraction for Secured PDFs and Distorted Word Documents

A small number of the 115 reports were in secured PDF formats, indicating that they could not be exported to a Word document for data extraction. Similarly, a small portion of unsecured PDFs did not successfully export to Word documents in a way in which data was easily identifiable or able to be extracted accurately (information was distorted). In both cases, this required manual data extraction from the PDF. To accomplish this, a secondary computer monitor was used, with the report PDF on one screen and the Excel file on the other. Data was manually imported into the Excel file by each PAH compound in each sample (e.g., phenanthrene for sample 1, pyrene for sample 1, and so on).

3.4.2 Non-Detect PAH Concentration Data

Given the utility of the substitution method for non-detect data among scientists and chemists in the environmental field, coupled with the similarity of a statistically robust method to a ½ detection limit (DL) substitution approach determined by MacAskill (2014), a ½ DL substitution method was applied to censor all non-detect data in this study. Thus, all non-detect data were replaced with values of ½ DL (specific to the reported DL in the individual MSSP and ESA reports). ½ DL values were subsequently used in aggregate PAH calculations (e.g., sum of high molecular weight PAHs, Total PAH_{16}).

In certain reports, specific PAHs had unique DL values, while other reports listed one DL for all PAHs in the report. All ½ DL values were computed specifically to the DL provided for that compound. To clearly identify data which was censored, all cells in the Excel files which were censored were kept white, while all cells which contained detectable concentrations of PAHs were highlighted in yellow.

3.4.3 Quality Assurance and Quality Control (QA/QC)

Quality assurance and quality control (QA/QC) approaches were implemented in data extraction and in data management as part of this study. QA represents a proactive process, while QC represents a reactive process. Specific to this study, quality assurance relates to the processes/actions which encouraged and promoted an accurate data set, while quality control relates to the processes/actions which inspected the data set to ensure it was indeed accurate. Both QA and QC were implemented to reduce the risk of errors in the data set. QA approaches that were implemented in this study included:

- All data sheets in this study were organized in the same way and uniquely named based on harbour and sampling date.
- When extracting data, only one sediment sampling report would be open at any given time. Once completed, reports were closed prior to the opening of another

report and the start of a new data sheet. This ensured that data could not be exported in duplicate.

- Consistent Excel computational commands (e.g., SUM) for were used throughout all data sheets to calculate LMW, HMW, and total PAH values.
- A data sheet template was created and used to ensure the computational commands of Excel remained consistent and were not re-typed.
- The organization of the Excel data sheets mimicked the organization of sediment sampling reports (e.g. the ordering of PAH compounds). This approach encouraged a large amount of data to be copied from the sampling report at a time, thereby reducing the error associated with exporting data to the Excel file in multiple segments.
- Conditional formatting in Excel was used to easily highlight sediment quality guideline exceedances.
- When importing data manually from PDFs, two computer monitors were used to support the highest level of accuracy.

QC approaches that were implemented in this study included:

- Each data sheet received a minimum 10% assessment for accuracy. To accomplish this, 5-10 random PAH concentration data cells were selected from the sampling report and were cross-referenced in the Excel file.
- All Excel computational commands were manually checked on every Excel sheet. Specifically, the computational command of SUM in Excel was tested once on each sheet by highlighting the cells used in the command and checking the sum provided in the bottom left corner of the Excel file.
- Conditional formatting was manually checked at random on every Excel sheet.

3.5 SEDIMENT QUALITY GUIDELINE COMPARISON FOR INDIVIDUAL PAHs

Individual PAH concentrations from each report were compared to Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs). Both types of CCME guidelines (ISQG, PEL) present values for 13 individual PAH compounds. To determine if individual PAHs in each sample were exceeding ISQG and PEL guidelines, conditional formatting in Excel was applied to each cell to depict three colours: green, yellow, or red. The colours indicated whether or not the PAH compound in the sample was below ISQG values (green), exceeded ISQG, yet below PEL (yellow), or exceeded PEL (red). An example of this approach is reflected in Table 3.3:

Table 3.3 An example of sediment quality guideline comparison formatting in Excel data management file.

	Sample ID (Concentration in mg/kg)			**Sediment Quality Guideline (mg/kg)**	
PAH Compound	***SC 16***	***SC 30***	***SC 51***	***CCME ISQG***	***CCME PEL***
Fluorene	0.01	0.09	0.01	0.0212	0.144
Naphthalene	0.005	0.005	0.005	0.0346	0.391
Phenanthrene	0.02	0.19	0.02	0.0867	0.544

As depicted in Table 3.3, the sediment sample identified as SC 30 consists of fluorene and phenanthrene concentrations (in mg/kg) which exceed ISQG values yet fall below PELs (yellow), while naphthalene falls below the ISQG concentrations (green). In contrast, sediment samples SC 16 and SC 51 demonstrate concentration values for fluorene, naphthalene, and phenanthrene that all fall below ISQGs, as depicted by their green colour. This approach was implemented for all 13 individual PAHs which had ISQG and PEL guideline values for each report. Conditional formatting facilitated determining the number of samples which had exceedances and which PAHs were most frequently causing these exceedances in each report, at the harbour level, or at the regional level. Summarized results from this approach were incorporated into Chapter 4.

$\sum PAH_{16}$ concentrations were also compared to National Oceanic and Atmospheric Administration (NOAA) effects range low (ERL) /effects range median (ERM) guidelines for total PAHs and Canadian Environmental Protection Act (1999) Disposal at Sea Guideline Regulation guidelines.

3.6 AGGREGATE PAH CONCENTRATION CALCULATIONS

The following aggregate summation (∑) PAH values were calculated for Chapter 4 (and one calculation for Chapter 5) using Excel AutoSum:

- Sum of Low Molecular Weight (LMW) PAHs: ∑ Ace, Acy, Ant, Fl, Nap, Phe
- Sum of High Molecular Weight (HMW) PAHs: ∑Pyr, Flu, BaA, BaP, BbF, BghiP, BkF, Chr, DbahA, IP
- Total PAH: ∑ all PAHs assessed in sample
- Total US EPA PAH_{16}: ∑ Nap, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DbahA, BghiP, IP
- ∑Flu, Pyr, Phe, Chr, B(b+k)F, BaA
- ∑Combustion PAHs [Flu, Pyr, BaA, BbF, BkF, BaP, DBahA, BghiP] **[Chapter 5]**

3.7 STATISTICAL ANALYSIS

3.7.1 Descriptive Statistics

Descriptive statistics were used to analyze, summarize, and interpret data in Chapter 4. All descriptive statistics were calculated by computational commands in Excel. Measures of frequency, measures of central tendency, and measures of dispersion were calculated for different aspects of the data set and included the following specific calculations:

Harbour-Specific Calculations

- $\sum PAH_{16}$ mean for each harbour (mg/kg)

- $\sum PAH_{16}$ range for each harbour (mg/kg)

Region-Specific Calculations

- Mean concentration of gravel, silt, sand, clay (%)
- Mean total organic carbon (TOC) and total inorganic carbon (TIC) (%)
- Relative abundance of individual US EPA 16 PAHs (%)

Entire Data Set Calculations

- Mean $\sum PAH_{16}$ for all SCHs combined (mg/kg)
- Standard deviation of mean $\sum PAH_{16}$ for all SCHs combined (mg/kg)
- Range of $\sum PAH_{16}$ for all SCHs combined (mg/kg)
- Mean, median, minimum, maximum, and standard deviation of 19 individual PAH concentrations (mg/kg)
- Count and percent of CCME ISQG/PEL exceedances for 19 PAHs
- Mean degree of difference for ISQG/PEL exceedances for 19 PAHs
- Standard deviation of mean degree of difference for ISQG/PEL exceedances for 19 PAHs
- Count and percent of National Oceanic and Atmospheric Administration (NOAA) effects range low (ERL) /effects range median (ERM) exceedances for $\sum PAH_{16}$
- Mean degree of difference for ERL/ERM exceedances for $\sum PAH_{16}$
- Standard deviation of mean degree of difference for ERL/ERM exceedances for $\sum PAH_{16}$

3.7.2 Analysis of Variance (ANOVA)

Two (separate) one-way analyses of variance (ANOVA) were completed using Minitab Statistical Software® to assess whether the mean of a variable demonstrated a statistical difference in groupings (Minitab Inc, State College, PA, 2010) in Chapter 4. The first ANOVA compared $\sum PAH_{16}$ concentrations among 31 SCHs. $\sum PAH_{16}$ concentration data was transformed ($\log_{10}$) to fulfill normality for this analysis. In the second ANOVA, TOC (%) was compared among the three DFO-SCH management regions (Gulf, Eastern, Southwest) to infer if this sediment characteristic varied among regions. For both analyses, Tukey’s multiple pairwise comparison was completed if the p-value from ANOVA was <0.05 (indicating that the difference between means was statistically significant) to determine if the differences between group pairs (e.g., SCH 1 *vs.* SCH 2, gulf *vs*. eastern) were statistically significant (Minitab Inc., 2017).

3.7.3 Pearson Correlation Analysis

To assess the linear relationship between variables, Pearson correlation analysis was completed for the following pairings in the respective manuscript chapters:

- $\sum PAH_{16}$ and TOC (%) [Chapter 4]
- $\sum$COMB PAHs [Flu, Pyr, BaA, BbF, BkF, BaP, DBahA, BghiP] and $\sum PAH_{16}$ [Chapter 5]

Pearson correlation analysis was conducted in Minitab Statistical Software® (Minitab Inc., State College, PA, 2010), with the understanding that the relationship between assessed variables would demonstrate a Pearson Correlation Coefficient that would fall between -1 and 1 (Minitab Inc., 2017). A negative number would be an indication of a negative relationship between the variables (one increases while the other does not), while a positive number would be an indication that the variables both increase or decrease concurrently. Values closer to 1 indicate a strong relationship, while direction of the relationship is indicated by either positive or negative (Minitab Inc., 2017). The following strength benchmarks for correlation analysis were adopted from MacAskill (2014) and used in this study such that values <0.3 indicate a weak relationship, values >0.8 indicate a strong relationship, and values between 0.3 and 0.8 indicate moderate strength. In the application of correlation analysis, it was understood that the identification of a relationship (correlation) between two variables does not indicate causation (Minitab Inc., 2017).

3.8 FORENSIC ASSESSMENT OF PAHs

Forensic assessment methodologies implemented as part of this study are organized into three lines of evidence that each contribute to addressing research objective two and are applied in Chapter 5. Methods were carefully selected to assess PAHs based on available data and include a mix of both quantitative and qualitative approaches. Forensic assessment methods implemented as part of this study include Unmix Optimum (Unmix O) modelling, PAH diagnostic ratios, and PAH profile composition assessment.

Unmix O addresses forensic assessment of PAHs in a quantitative-focused approach that applies a model to PAH concentration data to estimate PAH sources. Unmix estimates the number of sources that best characterize the data and provides insight into source compositions. PAH diagnostic ratios approach forensic assessment by using PAH concentration data and calculating ratios from pairs of PAHs with similar physicochemical properties (Tobiszewski and Namiesnik, 2012). This approach interprets results of these ratios by using values outlined (and widely adopted) in the literature that aid in source estimation (e.g., a ratio transitional value of 0.1 may be the transition value that distinguishes between petrogenic and pyrogenic PAH sources). PAH profile composition assessment in this study analyzes PAHs in two different ways- first, the assessment of PAHs on the basis of atomic rings (2-6 rings), and secondly, the assessment of combustion-associated PAHs as part of the PAH profile. This approach is more qualitative in that it aims to compare trends in the PAH profile that relate to larger trends in PAH source apportionment estimations. As such, these three methods are best represented as three separate, yet related techniques for the forensic assessment approach of PAHs used in this study.

3.8.1 PAH Diagnostic Ratios

Parent PAH double diagnostic ratios were selected for use in this study. Ratios were selected to ensure PAH pairs of different molecular masses were assessed. As such, one double ratio was selected for PAHs of the mass groupings of 178, 202, 228, and 276 g/mol. The ratios selected and applied in Chapter 5 are as follows:

- Mass 178: Anthracene/ (Anthracene + Phenanthrene)
- Mass 202: Fluoranthene/ (Fluoranthene+Pyrene)
- Mass 228: Benzo(a)anthracene/(Benzo(a)anthracene + Chrysene)
- Mass 276: Indeno(1,2,3-cd) pyrene/ (Indeno(1,2,3-cd) pyrene +Benzo(g,h,i) perylene)

An aggregate diagnostic ratio of ∑LMW/∑HMW PAHs was applied in Chapter 4 to estimate the dominance of petrogenic or pyrogenic sources (Hwang and Foster, 2006; Zhang et al., 2008). Similarly, the aggregate ratio of ∑4 ring /∑5+6 ring PAHs was applied as it supports whether PAHs are the product of localized inputs or the product of long-range transport (Liu et al., 2007; Souza et al., 2018).

3.8.2 Non-Detects and PAH Diagnostic Ratios

As PAH diagnostic ratios seek to estimate sources based on the ratio of the concentration of one PAH as compared to another, the use of censored data (or non-detects) poses concern (Helsel, 1990). The adoption of a ½ DL values for non-detects results in the potential for biased diagnostic ratios. For example, specific to this study, a large proportion of censored data read 0.0025 mg/kg, as 0.005 mg/kg was the most frequent DL. As such, adopting ½ DL values for <DL analytical results could hinder ratio accuracy, especially if one or both PAHs in the ratio being applied involve censored data. To determine the impact censored data would have on PAH diagnostic ratios, a comparative exercise was completed to assess the impact of including or excluding censored data. Figure 3.2 represents the PAH diagnostic ratio of Flu/(Flu+Pyr) vs. Ant/(Ant+Phe) with non-detects included (as ½ DL), while Figure 3.3 represents the same ratio with non-detects excluded. It is evident from comparison of Figures 3.2 and 3.3 that the presence of non-detects encourages clustering of data points near very low ratio values in the plot (i.e., close to 0), along horizontal values of 0.5, and along vertical values of 0.6. As a result, an increased number of data points fall in plot areas defined as "*petroleum*" and "*combustion*" by Yunker et al. (2002). Numerically, the exclusion of non-detects reduced the number of data points included in the plot by 60, and

subsequently impacted the distribution of these points in plot areas defined by Yunker et al. (2002) (Table 3.4).

PAH diagnostic ratio interpretation seeks to identify clusters, as they can be an indication of prominent source(s) (Tobiszewski and Namieśnik, 2012). As such, the use of censored data can negatively hinder this interpretation as it can create clusters that are mainly an indication of censorship and that do not accurately reflect the data. Subsequently, it strongly complicates the interpretation of diagnostic ratios and can lead to poorly defined estimations of PAH sources. Therefore, to account for this issue, all parent PAH diagnostic ratio plots applied in this study used detectable concentrations of PAHs (>DL) only.

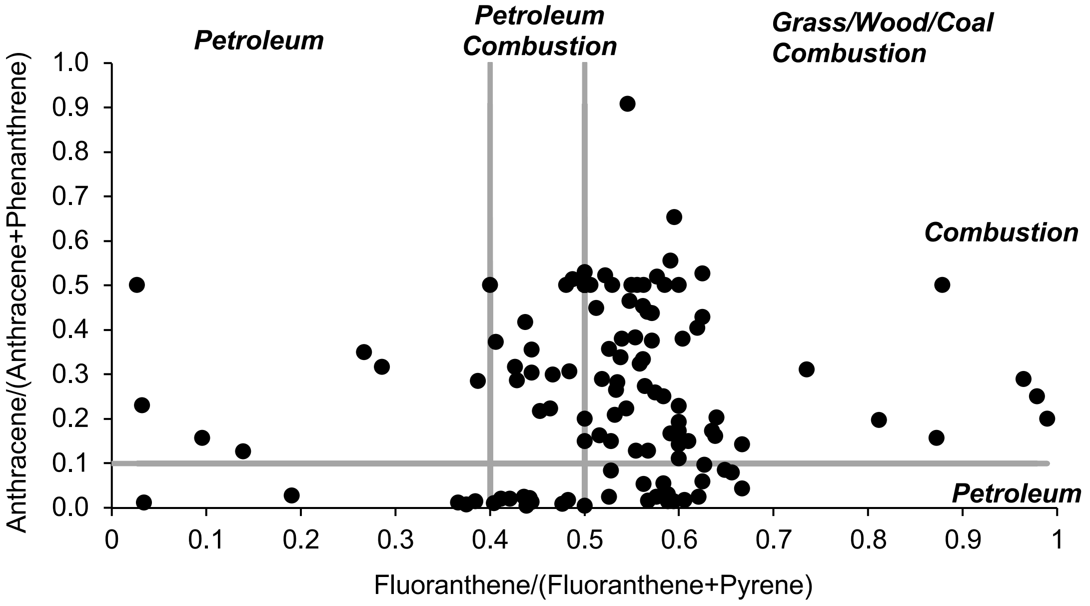

Figure 3.2 PAH diagnostic ratio plot with censored data (*n*=126).

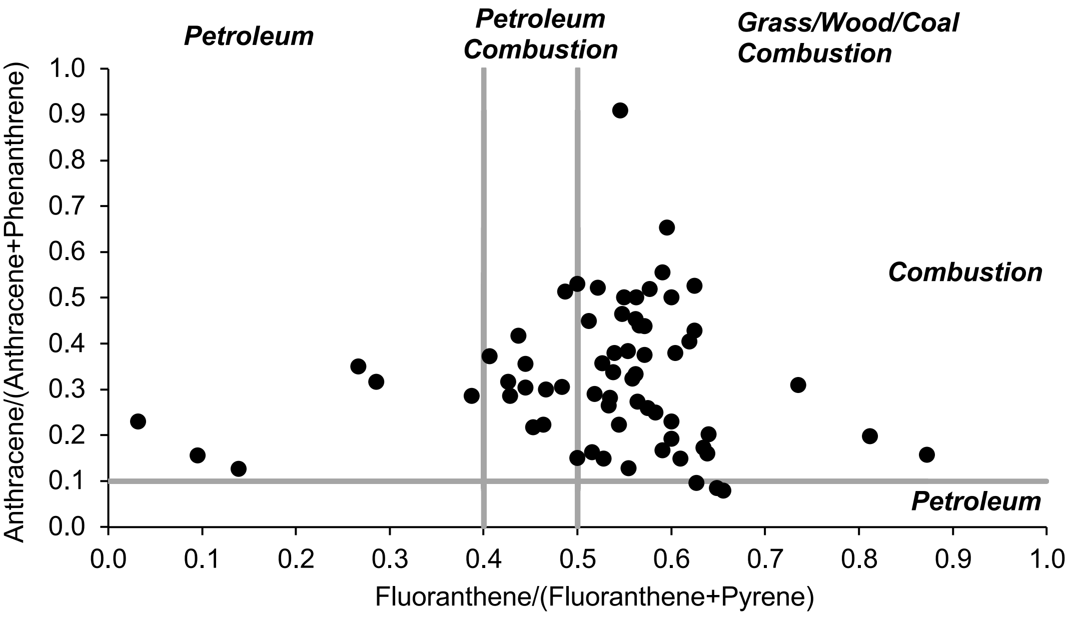

Figure 3.3 PAH diagnostic ratio plot without censored data (*n*=66).

Table 3.4 Numerical assessment of PAH diagnostic ratio estimated sources with and without non-detect data points.

Estimated Source	**Non-Detects In (%) (*n*=126)**	**Non-Detects Out (%) (*n*=66)**
Petroleum	30.16	13.64
Petroleum Combustion	10.32	19.70
Combustion	59.52	66.67

3.8.3 Unmix Optimum (Unmix O)

Unmix O was selected as a multivariate receptor model and applied in Chapter 5 of this study. Unmix O was selected as a viable model as it was developed to compensate for issues associated with other multivariate receptor models and it did not require previous knowledge of PAH sources impacting sediment samples. The application of Unmix O was novel as it has not been widely used in Canada and has yet to be applied to sediment data in the province of NS. An additional benefit to applying this model was the opportunity to support US EPA assessment of the Unmix model. Technical guidance was provided by the US EPA.

The Unmix O model was applied to the data in Chapter 5 with the following model-specific considerations in place:

- Constrained non-linear optimization algorithm
- Loose tolerance level (constraint level 1.1)
- Model error level of 15% (as per a Monte Carlo method for multivariate models (Timmerman et al., 2007))
- A total of 509 observations were included in the model
- PAHs included in the model (*n=14*): acenaphthene (Ace), anthracene (Ant), Benzo(a) anthracene (BaA), benzo(a)pyrene, benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(ghi)perylene (BghiP), chrysene (Chr), fluoranthene (Flu), fluorene (Fl), indeno(1,2,3-cd) pyrene (IP), phenanthrene (Phe), pyrene (Pyr)
- 1 and 2-methylnaphthalene (1-MN and 2-MN) and perylene (Per) were excluded due to a high number of missing data points
- Acenaphthylene (Acy), dibenz(ah)anthracene (DbahA) and naphthalene (Nap) were excluded as they negatively impacted model fit by outlier data points. Initial tests confirmed that these compounds demonstrated outlier concentrations that hindered the model's ability to best define sources and source compositions

3.8.4 PAH Profile Composition Assessment

PAH profile composition assessment applied in Chapter 5 of this study seeks to determine trends from the PAH profile that can be an indication of PAH source emissions. The term "PAH profile" in this study represents the collective PAHs assessed in sediment (19 PAHs are typically assessed in reports). Specifically, this approach organizes the PAH profile into defining characteristics. Defining characteristics of the PAH profile include the number of atomic rings, categorization based on LMW or HMW (molecular weight), and if PAHs are associated with "combustion" emission processes. PAH profile composition assessment in this study was completed in two different ways.

First, the distribution of 2-6 ring PAHs was completed for each region (Gulf, Eastern, Southwest). To accomplish this, PAHs were grouped by the number of atomic rings they possess. The concentration of each grouping (2-6 rings) was calculated (mg/kg) in Excel for every individual sample. Following this, the concentration of each ring group was compared to the concentration of all PAHs and calculated as a percent of total PAHs. Samples for harbours within the management regions were summarized regionally and the average proportion of each ring group was calculated. PAH profile composition was also assessed by calculating the aggregate concentration of individual PAHs that are deemed "combustion" produced PAHs from the literature (Prahl and Carpenter, 1983). Combustion produced PAHs are the following: Flu, Pyr, BaA, BbF, BkF, BaP, DBahA, BghiP (Prahl and Carpenter, 1983).

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CHAPTER 4

CHARACTERIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SMALL CRAFT HARBOUR (SCH) SEDIMENTS IN NOVA SCOTIA, CANADA*

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) have been widely studied in sediments due to their ubiquity and persistence in aquatic environments and potential for impairment to biota. Small craft harbour (SCH) sediments in Nova Scotia (NS), Canada, have yet to be studied comprehensively. SCHs are essential to the fishing industry, which is important for the Canadian economy. This spatiotemporal characterization study evaluated thirty-one SCHs across NS between 2001-2017 by analyzing sediment reports (secondary data). Sediment PAH concentrations varied widely across all SCHs. Few SCHs exhibited sediment PAH concentrations likely to impair biota based on comparison to sediment quality guidelines. Sediments in the Gulf region of NS were least contaminated by PAHs, while the Southwest region was most contaminated. Distribution of individual PAHs in sediments follows global trends, with high molecular weight PAHs dominating samples.

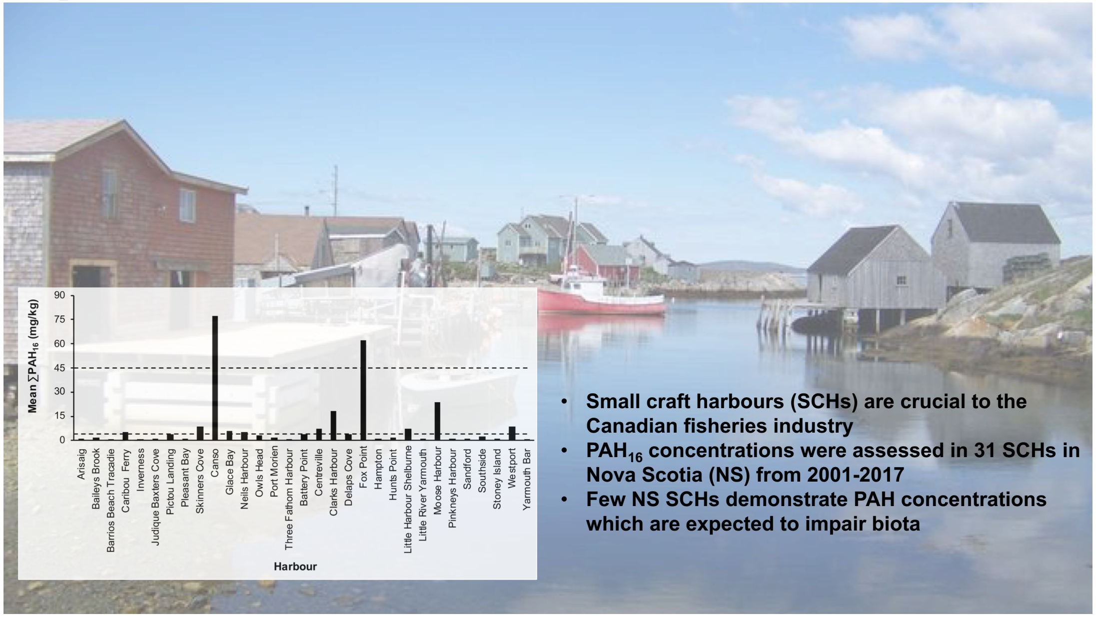
Key words: Polycyclic aromatic hydrocarbons (PAHs); Small craft harbour (SCH) sediments; Sediment quality guidelines (SQGs); Nova Scotia (NS)

Highlights:

- Sediment $\sum PAH_{16}$ concentrations were spatiotemporally characterized in 31 NS SCHs spanning 17 years
- Sediment $\sum PAH_{16}$ concentrations ranged between 0.037-336.770 mg/kg
- Only two SCHs exhibited mean $\sum PAH_{16}$ concentrations expected to impair biota (>NOAA ERM guideline)
- Sediment $\sum PAH_{16}$ concentrations provide valuable information for SCH characterization
- Six individual high molecular weight PAH compounds dominate NS SCH sediments

* *Prepared as an article for Marine Pollution Bulletin and published October 20, 2018*

Graphical Abstract:



- Small craft harbours (SCHs) are crucial to the Canadian fisheries industry
- PAH_{16} concentrations were assessed in 31 SCHs in Nova Scotia (NS) from 2001-2017
- Few NS SCHs demonstrate PAH concentrations which are expected to impair biota

4.1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) represent one class of hydrophobic organic contaminants found in aquatic environments all over the world (Lima et al., 2005; Manariotis et al., 2011). On a global scale, elevated PAH contamination in sediments is often associated with aquatic sites located near current or former industrial activities, or near urban centers, due to increased likelihood of anthropogenic inputs of PAHs from surrounding environments (Viguri et al., 2002; Ke et al., 2005; Jiang et al., 2009). PAHs can enter aquatic environments from a variety of different sources and are often categorized into three main types: petrogenic, pyrogenic, and natural (Jiang et al., 2009). Petrogenic PAHs occur from petroleum hydrocarbons, pyrogenic PAHs are derived from the combustion of fossil fuels and biomass, while natural sources of PAHs are derived from forest fires, diagenesis, and natural petroleum seeps (McCready et al., 2000; Mahanty et al., 2011; Masood et al., 2016). PAH compounds which enter into aquatic environments are often anthropogenic in origin and occur primarily from combustion (pyrogenic) sources (Wang et al., 2001; Lima et al., 2005; Stout et al., 2015).

PAHs are of particular environmental concern as they can exhibit carcinogenic and/or mutagenic properties and can bio-accumulate in aquatic food chains (Fang et al., 2012; Stout et al., 2015). Given the hydrophobic and persistent characteristics of PAHs, they easily sorb to sediment and can remain in aquatic environments for long periods of time, thereby presenting a risk to aquatic species (Liu et al., 2013b; Wu et al., 2014; Li et al., 2015). Aquatic species are exposed to PAHs through feeding and water uptake, or by encountering PAHs in sediments or pore water (Kupryianchyk et al., 2012). Dissolved PAH compounds in the aqueous phase, or in sediment pore water, are more bioavailable to aquatic species as compared to PAHs which are tightly bound to sediment particles (Neff et al., 2005). PAHs from sediment can impact humans, if consumption of exposed aquatic species occurs (Jiang et al., 2009).

Given potential adverse effects of PAHs, these compounds are considered contaminants of concern around the world (Katsoyiannis and Samara, 2005; Stout et al., 2015). The United States Environmental Protection Agency (US EPA) has classified 16 individual PAH compounds as priority pollutants ($\sum PAH_{16}$), and seven PAHs as probable human carcinogens, while the National Oceanic and Atmospheric Administration (NOAA) has outlined risk-based benchmark values for PAH concentrations (Long et al., 1995; US EPA, 2014; Van Metre and Mahler, 2014). Similarly, in Canada, the Canadian Council of Ministers of the Environment (CCME) have outlined environmental quality guidelines which state specific benchmarks for some PAHs in soil, water, tissue, and sediment (CCME, 2014).

Contamination inputs to sediments has been recognized as an important issue for decades (Larsson, 1985; Hong et al., 1995; Lima et al., 2005). However, variation in presence, magnitude, and extent of contaminants in sediments has been demonstrated in the literature globally (Ke et al., 2005; Lima et al., 2005; Walker et al., 2013b). Coastal Nova Scotia (NS), Canada, is not immune to this issue. Two prominent and highly publicized examples of sediment contamination in Nova Scotia marine environments include Halifax Harbour and Sydney Harbour, both of which are considered large harbours and currently serve as important commercial and tourism-related harbours for the region (Robinson et al., 2009; Walker et al., 2013b,c, 2015a; Walker and MacAskill, 2014; MacAskill et al., 2016). Halifax Harbour, due to a historical influx of untreated sewage and wastewater, has shown an elevated presence of organic estrogenic contaminants (bisphenol A, estradiol) in sediment (Robinson et al., 2009). Similarly, high levels of polychlorinated biphenyls (PCBs), PAHs, and metals have been detected in Sydney Harbour sediment samples, suggested to be associated with anthropogenic inputs from a coking and steel plant that used to operate near the harbour (Walker et al., 2013c).

NS is home to 178 (core and non-core) fishing small craft harbours (SCHs) which are crucial to the success of the NS fishing industries (DFO, 2016). NS fisheries play an important economic role for the Canadian fishing industry (valued at CAD $3.3 billion in 2016), as they contribute the greatest live weight landings among all provinces (DFO, 2018b). SCH sites, which directly support the vessels which gather various commercial fish species, are scattered along the NS coastline and are often located in rural communities (Walker et al., 2013a). Certain SCH sites are managed and owned by the Fisheries and Oceans Canada Small Craft Harbour branch (DFO-SCH). SCHs are typically smaller than Canadian commercial ports, however; sediments in SCHs are subjected to potential anthropogenic contaminant inputs from varying historical and ongoing sources. Given the federal environmental and financial liability of SCHs in Canada, and the widely documented environmental and human health risks of PAH compounds, it is important to evaluate magnitude and extent of PAH contamination within SCHs (Walker et al., 2015b). Despite a plethora of monitoring reports conducted at individual SCHs, a comprehensive spatial and temporal assessment of PAHs at SCH sites has not been completed.

Specific objectives of this study were to:

a) Determine distribution of PAH concentrations across the Gulf, Eastern, and Southwestern regions of NS, by assessing 31 SCHs temporally over 17 years.
b) Evaluate PAH concentrations through comparison to Canadian sediment quality guidelines (SQGs) and those derived from other jurisdictions.
c) Examine abundance and distribution of PAH compounds across SCHs.

4.2 MATERIALS AND METHODS

4.2.1 SCH Selection

This study evaluated 31 SCHs across three DFO-SCH management regions of NS (Table 4.1; Fig. 4.1). All SCHs are core fishing harbours, according to DFO classification of SCH sites. SCHs were selected for this study based on a previous assessment of cost-effective sediment dredge disposal options for priority SCHs in NS (Walker et al., 2013a). Walker et al. (2013a) reviewed historical marine sediment sampling reports (MSSPs) for 35 SCHs from NS, reporting detectable concentrations of PAHs and other contaminants. The 31 SCHs selected were selected in part by the list of 35 sites listed, alongside consultation and discussion with federal custodians of NS SCHs. SCHs which did not have more than one MSSP available were excluded from the selection. SCHs in NS fall into three different management regions (Fig. 4.1) under DFO-SCH: Gulf, Eastern and Southwest (Walker et al., 2013a). To gather historical data across the entire province, SCHs from all three DFO-SCH management regions were selected. In total, nine SCHs were selected from the Gulf region, six from the Eastern region, and 16 from the Southwestern region.

Table 4.1 Assessed SCHs in NS, organized by the region in which they reside. Harbours are identified by sequential numbers (1 through 31).

Gulf NS (Harbours 1-9)	**Eastern NS (Harbours 10-15)**	**Southwest NS (Harbours 16-31)**
1. Arisaig	10. Canso	16. Battery Point
2. Baileys Brook	11. Glace Bay	17. Centreville
3. Barrios Beach Tracadie	12. Neils Harbour	18. Clarks Harbour
4. Caribou Ferry	13. Owls Head	19. Delaps Cove
5. Inverness	14. Port Morien	20. Fox Point
6. Judique Baxters Cove	15. Three Fathom Harbour	21. Hampton
7. Pictou Landing		22. Hunts Point
8. Pleasant Bay		23. Little Harbour Shelburne
9. Skinners Cove		24. Little River Yarmouth
		25. Moose Harbour
		26. Pinkneys Point
		27. Sandford
		28. South Side
		29. Stoney Island
		30. Westport
		31. Yarmouth Bar

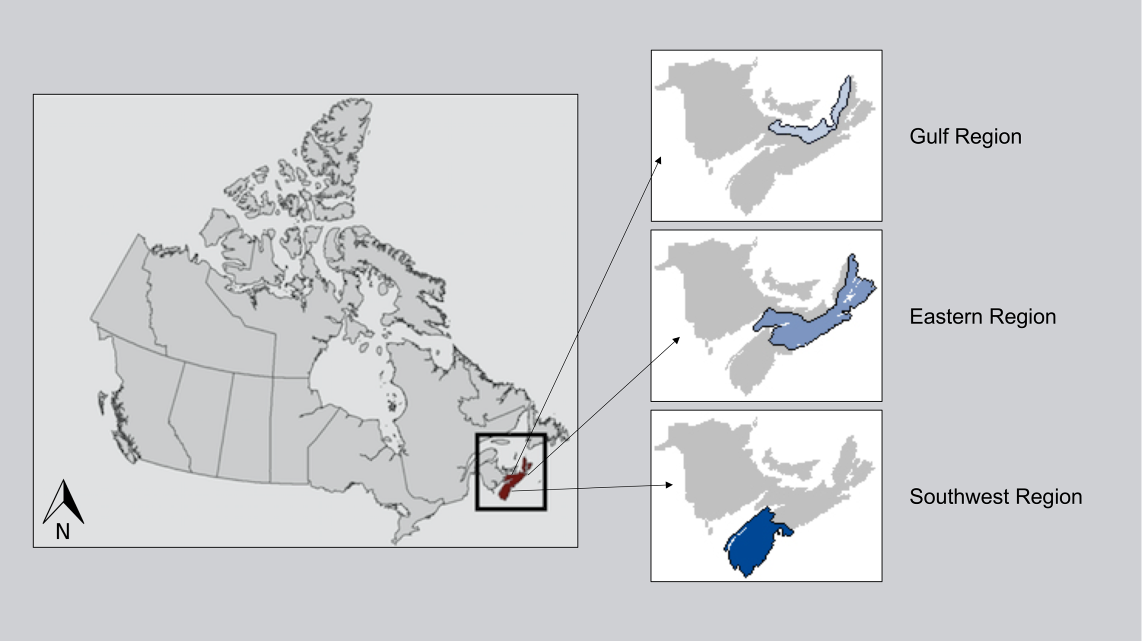


Figure 4.1 Location of DFO-SCH management regions in Nova Scotia. Regional figures are adapted from Fisheries and Oceans Canada (DFO, 2018c). [Map produced by DMTI™].

4.2.2 Historical Sediment Data

SCH sediment data was provided by Public Service and Procurement Canada (PSPC) on behalf of DFO-SCH. Majority of data originated from Marine Sediment Sampling Program (MSSP) reports between 2001-2017 for DFO-SCH, alongside 10 Environmental Site Assessments (ESAs). PSPC is responsible for overseeing completion of MSSPs for DFO-SCH, to satisfy management strategies and mandates for SCHs. MSSP reports are completed for SCHs prior to dredging activities to provide harbour decision makers with sediment quality information to inform dredged sediment disposal options. MSSPs are used to characterize sediment contamination within proposed dredging boundaries at SCHs. MSSPs are designed to collect sediment samples and compare samples to environmental quality guidelines, most often outlined by the Canadian Council of Ministers of the Environment (CCME). Sediment samples from both MSSPs and ESAs are commonly collected as surficial grab samples (0-10 cm horizon) and occasionally using cores (Walker et al., 2013a). Contaminants typically assessed in MSSPs include:

PAHs, total petroleum hydrocarbons, metals, PCBs, dichloro-diphenyl-trichloroethane (DDT), and benzene, toluene, ethyl benzene, and xylenes (BTEX).

MSSPs are routinely completed following DFO-SCH mandates to ensure physical navigation for boat traffic (Walker et al., 2013a). All harbours evaluated as part of this study demonstrated a minimum of two sampling intervals (two MSSP and/or ESA reports) between 2001-2017 (Appendix B). The frequency of MSSP intervals at each SCH varied due to differences in dredging requirements. Sediment samples varied between three and eight samples per MSSP/ESA. A total of 580 sediment samples were used in this assessment. Physicochemical characteristics of these sediments are summarized (Table 4.2).

Table 4.2 Regional summary of SCH sediment physicochemical characteristics across NS. All characteristics (grain size, total organic carbon (TOC), total inorganic carbon (TIC)) are reported as mean values for each region with standard deviation in parentheses.

Region of NS	**Reports (#)**	**Samples (#)**	**Gravel (%)**	**Sand (%)**	**Silt (%)**	**Clay (%)**	**TOC (%)**	**TIC (%)**
Gulf	45	224	8.10 (15.14)	49.99 (31.84)	30.60 (23.95)	14.39 (11.85)	2.87 (12.53)	0.44 (0.49)
Eastern	19	108	10.61 (14.72)	49.32 (25.29)	34.10 (23.21)	11.31 (8.66)	4.06 (7.78)	1.08 (1.44)
Southwest	51	248	17.76 (22.10)	54.39 (24.49)	25.00 (20.52)	9.69 (8.56)	1.83 (2.16)	0.81 (0.82)

4.2.3 Sediment Quality Guideline (SQG) Comparison

SQGs are valuable in assessment of sediment chemistry data, as they provide concentration benchmarks to assist interpretation of potential ecological risk (Long and MacDonald, 1998; Long et al., 1998; Birch, 2018). SQGs are derived using a weight of evidence approach, often using both chemistry and biological approaches in their derivation (MacDonald et al., 1996; Long et al., 1998; Birch, 2018). Effects based guidelines aim to identify concentration values in which adverse effects are likely to occur for biota. These guidelines are often presented as effects range low (ERL), effects range median (ERM), or probable effect levels (PELs). ERL values represent the lower

10th percentile for a concentration, while the ERM reflects the median (50th percentile) for a concentration within effects analyses (Long et al., 1998). If concentration values fall below an ERL, adverse effects are rarely to occur. If values fall between ERL and ERM guidelines, adverse effects may occasionally occur. Lastly, if values exceed ERM guidelines, the likelihood of adverse biological effects is expected to be frequent (MacDonald et al., 1996; Long et al., 1998).

In Canada, Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs) were developed by the CCME for the protection of aquatic life in both marine and freshwater systems (CCME, 2014). The derivation of SQGs in Canada are built on approaches from the NOAA National Status and Trends Program (NSTP) and spiked-sediment toxicity test (SSTT) (CCME, 1995). The NSTP provides insight to contaminant concentrations and biological effects over time from many sites across the United States (O'Connor and Ehler, 1991; CCME, 1995). CCME ISQG's and PELs are similar to effect level values in that the ISQG value is representative of a low effects range, while PELs are an indication at which adverse effects are frequently to occur—similar to effects range [median] values (Walker et al., 2015a).

PAH concentrations in SCH sediments were compared to SQGs including: CCME ISQGs and PELs, and NOAA ERL and ERM values. NOAA outlines ERL and ERM values for individual PAH compounds and values for total PAHs (Long et al., 1995; Long and MacDonald, 1998). As PAH compounds are released into the environment as mixtures, ∑PAH concentrations and their respective SQGs prove useful as a coarse screening tool for evaluating PAHs in sediments (Long and MacDonald, 1998). This is supported by the various biological and chemical analyses used in the derivation of ERL and ERM values that often-employed mixtures of contaminants to help provide insight to "real world" situations (Long and MacDonald, 1998).

4.2.4 Data and Statistical Analysis

Descriptive statistics were completed in this study and included measures of frequency (counts, percent), measures of central tendency (mean, median), and measures of variation (range, standard deviation). The following PAH data were considered in analysis:

- Concentration of individual PAHs (mg/kg dry weight)
- Sum of US EPA 16 Priority PAHs ($\sum PAH_{16}$)
- Sum of ∑Flu, Pyr, Phe, Chr, B(b+k)F, BaA

Detection limits (DLs) for individual compounds varied, with DL values ranging between 0.01 and 0.008 mg/kg. If PAH concentrations fell beneath the DL, a ½ DL value was adopted and used in analyses (MacAskill et al., 2016). Analytical DLs for PAHs did change (shifted to lower values) during the temporal period (2001-2017) and reports reflect the lowest DLs available for PAHs (at the laboratory completing the analysis) in a given sampling year.

To evaluate relationships between $\sum PAH_{16}$ and physicochemical sediment characteristics, Pearson correlation analysis was completed in Minitab Statistical Software® (Minitab Inc, State College, PA, 2010). ANOVA was employed to compare $\sum PAH_{16}$ concentrations among SCHs, and to compare TOC (%) among regions. Tukey's multiple pairwise comparison was used if appropriate ($p<0.05$). $\sum PAH_{16}$ sediment data was transformed ($\log_{10}$) to satisfy normality. Minitab Statistical Software® was used for analysis (Minitab Inc, State College, PA, 2010) and significance was reported if the *P* value was less than the significance level ($\alpha=0.05$).

4.2.5 Quality Control

All MSSP sediment samples (including blind field duplicates) were analyzed by commercial laboratories (Standards Council of Canada accredited) for analysis of PAHs (dw) basis, unless otherwise indicated. Method blanks, spike blanks, matrix spikes, duplicate samples, and quality control protocols varied, so individual reports are cited for more detailed information.

4.3 RESULTS AND DISCUSSION

4.3.1 Sediment Characteristics: Grain Size, TOC (%)

Table 4.2 displays different physicochemical characteristics of SCH sediments. Mean values were determined from all samples within a region. All three regions display a higher percentage of coarse grained particles (gravel and sand) compared to finer grained particles (silt and clay). Grain (particle) size can influence how PAHs behave in aquatic environments (Karickhoff, 1979), as finer grained sediments more easily accumulate and hold PAHs, making them less bioavailable to aquatic species (Xia et al., 2013; Zhang et al., 2014; Lai et al., 2015).

Sediment TOC can also influence PAH behavior in aquatic environments and has been widely studied (Karickhoff, 1979; Jiang et al., 2009; Wang et al., 2011). Carbon assists in stabilizing PAHs, as they bind tightly to these particles in sediment and are therefore unable to migrate into the water column (Koelmans et al., 2006). Mean TOC across the regions ranges from 18.31 to 40.28%. However, regions are statistically similar to one another in terms of mean TOC (%) (*P*-value: 0.083). Correlation analysis assessed the relationship between $\sum PAH_{16}$ and TOC (%) of sediments across all 31 SCHs combined. An extremely weak positive relationship was observed between $\sum PAH_{16}$ and TOC (%) (Pearson correlation: 0.103, *P*-value: 0.036). It is likely that this relationship is influenced by many other factors, including: sampling depth, grain size distribution, and other harbour-specific characteristics (location, use, history). Furthermore, the weak relationship between PAHs and TOC above may be an indication that TOC does not play a large role in the presence and stabilization of PAHs in NS SCHs (Shi et al., 2007). Similarly, Fang et al (2007) indicate that particle grain size may play a stronger role in the stabilization of PAHs, as compared to TOC, particularly in areas which demonstrate high levels of PAH contamination. It is likely that both TOC and particle grain size contribute to the behavior of PAHs in NS SCH sediments, but the inter-relationships of these physicochemical characteristics and their impact on PAHs is difficult to define.

4.3.2 Mean ∑PAH$_{16}$ Comparison among SCHs and to SQGs

Mean ∑PAH$_{16}$ was calculated for each SCH, by combining all sediment samples between 2001-2017 and assessing the US EPA priority PAHs (16). To determine the risk in which sediments may pose to biota, concentrations were compared to NOAA ERL and ERM guidelines and CEPA (1999) Disposal at Sea Regulation Guidelines (CEPA, 1999). Fifteen SCHs (48.4%) exhibit mean ∑PAH$_{16}$ values below CEPA (1999) Disposal at Sea Regulations guideline of 2.5 mg/kg for ∑PAHs. These 15 SCHs are formed from 6, 2, and 7 SCHS in the Gulf, Eastern, and Southwest regions, respectively (Fig 4.2)

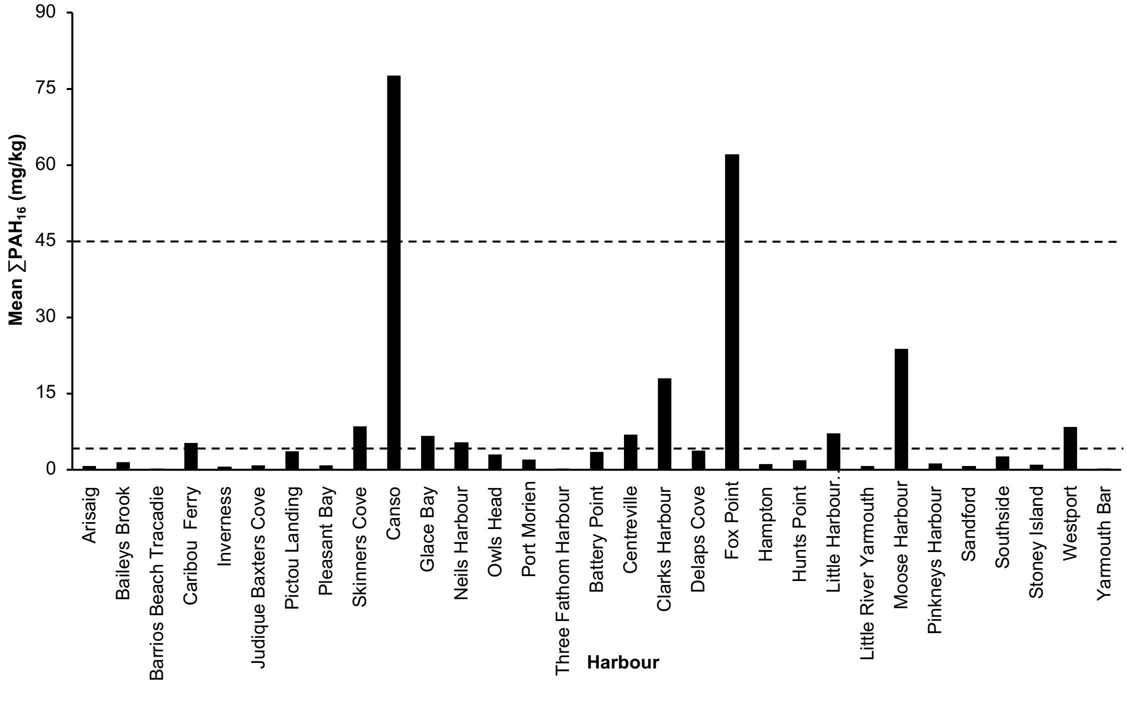


Figure 4.2 Mean ∑PAH$_{16}$ concentrations in sediments of NS SCHs. Lower dashed horizontal line represents NOAA ERL guideline for total PAHs (4.022 mg/kg), upper horizontal line represents NOAA ERM for total PAHs (44.792 mg/kg).

Twenty SCHs (64.5%) exhibit mean ∑PAH$_{16}$ values below NOAA ERL (4.022 mg/kg), an indication that adverse effects are rarely to occur for biota (Figs. 4.2 and 4.3). Of these 20 SCHs, seven occur in the Gulf region, three in the Eastern, and 10 in the Southwest region. Nine SCHs exhibit mean ∑PAH$_{16}$ values which exceed the ERL benchmark yet fall below the ERM benchmark (44.792 mg/kg). Of these nine, two are located in both the Gulf and Eastern regions, while five are located in the Southwest. $\sum$PAH values between the ERL and ERM indicate that adverse effects may occasionally occur for biota. Canso harbour in Eastern region (*n*=12), and Fox Point (*n*=6) from the southwest demonstrate the highest mean $\sum PAH_{16}$ among all SCHs with 77.576 and 62.120 mg/kg, respectively (Figs. 4.2 and 4.3). Mean $\sum PAH_{16}$ for Canso and Fox Point exceed the NOAA ERM, suggesting that the likelihood of impairment to biota is expected to be frequent (Fig. 4.3).

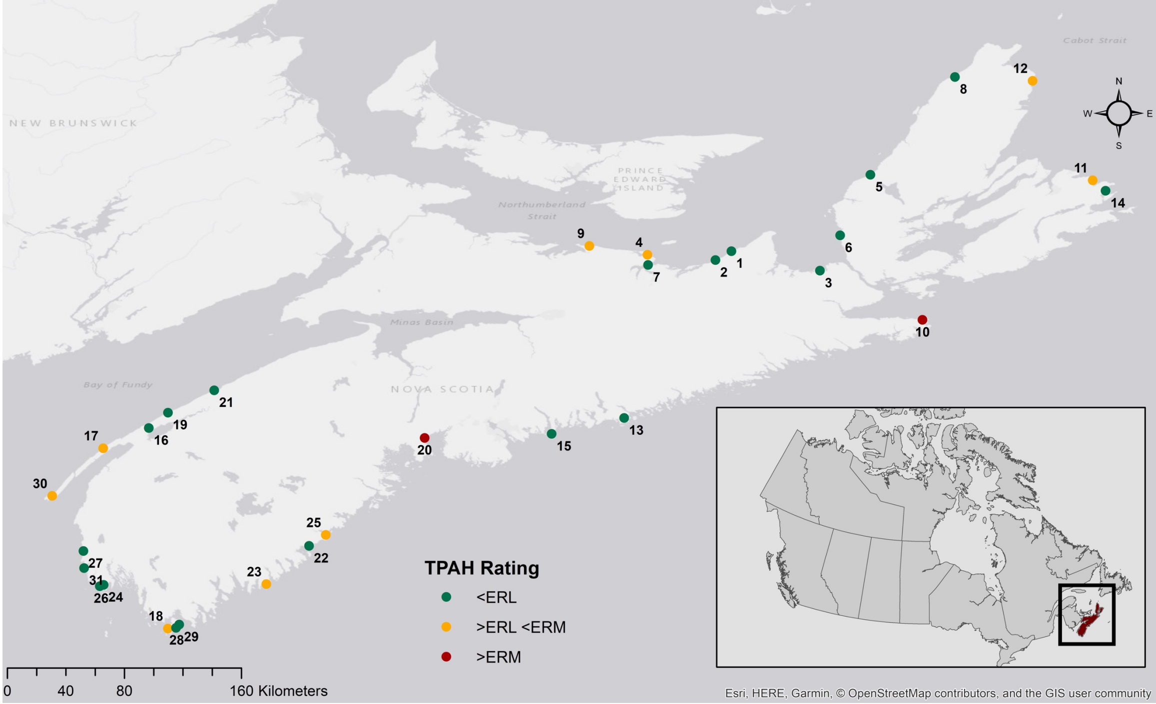


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Figure 4.3 Spatial distribution of selected SCHs across NS. SCHs are organized by mean $\sum PAH_{16}$ concentrations as a comparison to NOAA sediment quality guidelines (SQGs) (ERL and ERM) [Inset map of Canada was produced by DMTI™].

Mean $\sum PAH_{16}$ concentrations among SCHs were compared by ANOVA. A significant difference among mean $\sum PAH_{16}$ concentrations among SCHs was determined ($P<0.000$). Tukey's multiple pairwise test indicated that 16 of 31 SCHs were statistically similar to one another. Canso and Fox Point, which have the highest mean PAH concentrations, are statistically similar to one another, and to five other harbours of the same statistical grouping: Moose Harbour, Clarks Harbour, Westport, Centreville, and Neils Harbour. This analysis indicates that many NS SCHs demonstrate PAH contamination levels which are similar to one another, and that those which are most heavily contaminated are limited to seven of the 31 sites.

Of the total number of sediment samples (*n*=580), 124 samples (21.4%) exceeded the ERL for $\sum PAH_{16}$ and 18 of those samples (3.1%) exceeded the ERM for $\sum PAH_{16}$ (Table 4.3). The eighteen samples which exceeded the ERM were distributed among the following SCHs: Skinners Cove (*n*=1), Canso (*n*=4), Glace Bay (*n*=2), Clarks Harbour (*n*=1), Delaps Cove (*n*=1), Fox Point (*n*=3), Little Harbour Shelburne (*n*=1), Moose Harbour (*n*=5). 11 of these 18 samples which exceeded the ERM were concentrated to the Southwest region, further solidifying that the Southwest region is most contaminated by PAHs.

Table 4.3 CCME (Interim Sediment Quality Guidelines (ISQG) and Probable Effect Level (PEL)) and NOAA (Effects Range Low (ERL) and Effects Range Median (ERM)) sediment quality guideline (SQG) exceedances and degree of difference for select PAH compounds and total PAH_{16} in NS SCH sediments between 2001-2017.

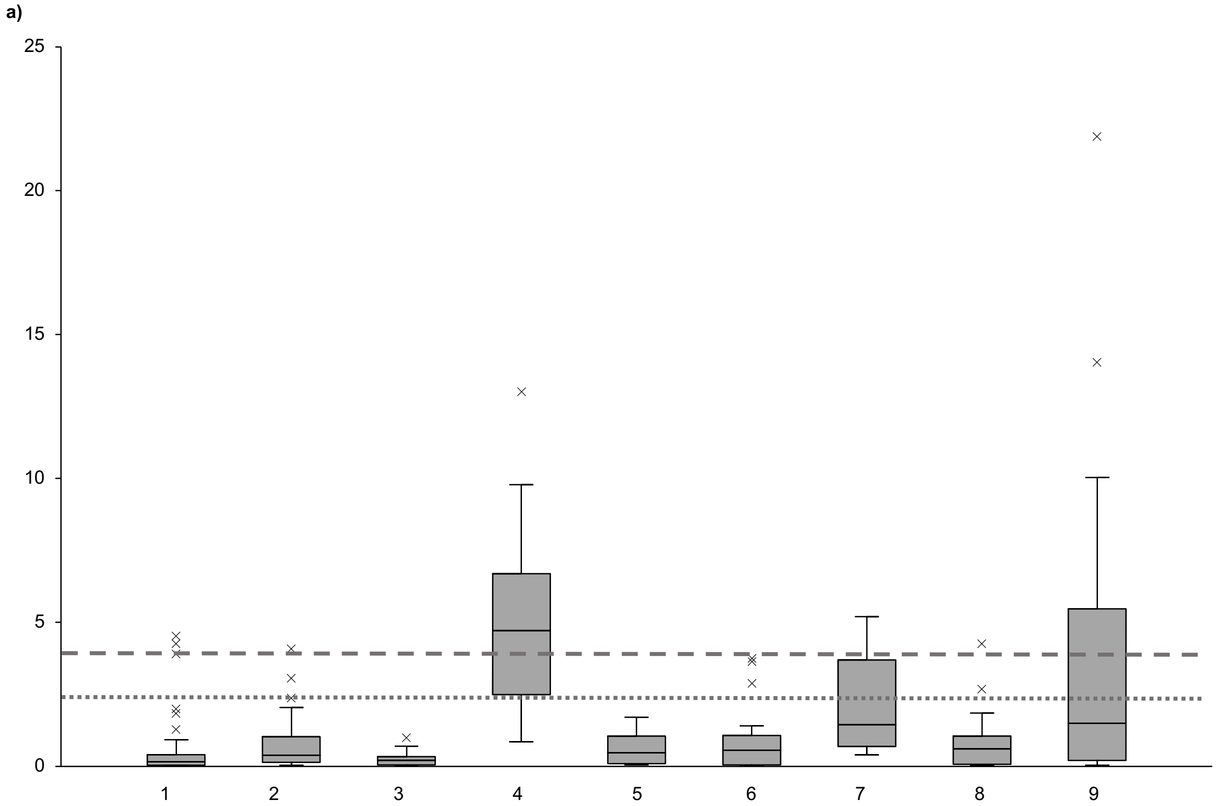
Parameter (*n*=580)	**CCME Marine SQG**					
	ISQG			**PEL**		
	SQG (mg/kg)	# of exceedances (%)	Mean Degree of Difference (+/- SD)	SQG (mg/kg)	# of exceedances (%)	Mean Degree of Difference (+/- SD)
Naphthalene	0.0346	80 (13.8)	2.48 (2.20)	0.391	15 (2.6)	7.67 (10.79)
2-Methylnaphthalene	0.0202	161 (27.8)	1.23 (2.04)	0.201	31 (5.3)	3.88 (7.92)
Acenaphthylene	0.00587	199 (34.3)	3.91 (3.04)	0.128	17 (2.9)	2.54 (7.11)
Acenaphthene	0.00671	270 (46.6)	3.09 (2.05)	0.0889	45 (7.8)	12.90 (30.27)
Fluorene	0.0212	225 (38.8)	1.18 (1.45)	0.144	58 (10.0)	6.81 (14.87)
Phenanthrene	0.0867	161 (27.8)	1.69 (1.38)	0.544	75 (12.9)	6.26 (17.84)
Anthracene	0.0469	126 (21.7)	1.51 (1.18)	0.245	93 (16.0)	5.25 (11.99)
Fluoranthene	0.113	260 (44.8)	3.03 (2.95)	1.494	82 (14.1)	4..45 (11.04)
Pyrene	0.153	198 (34.1)	2.22 (2.01)	1.398	63 (10.9)	4.04 (8.82)

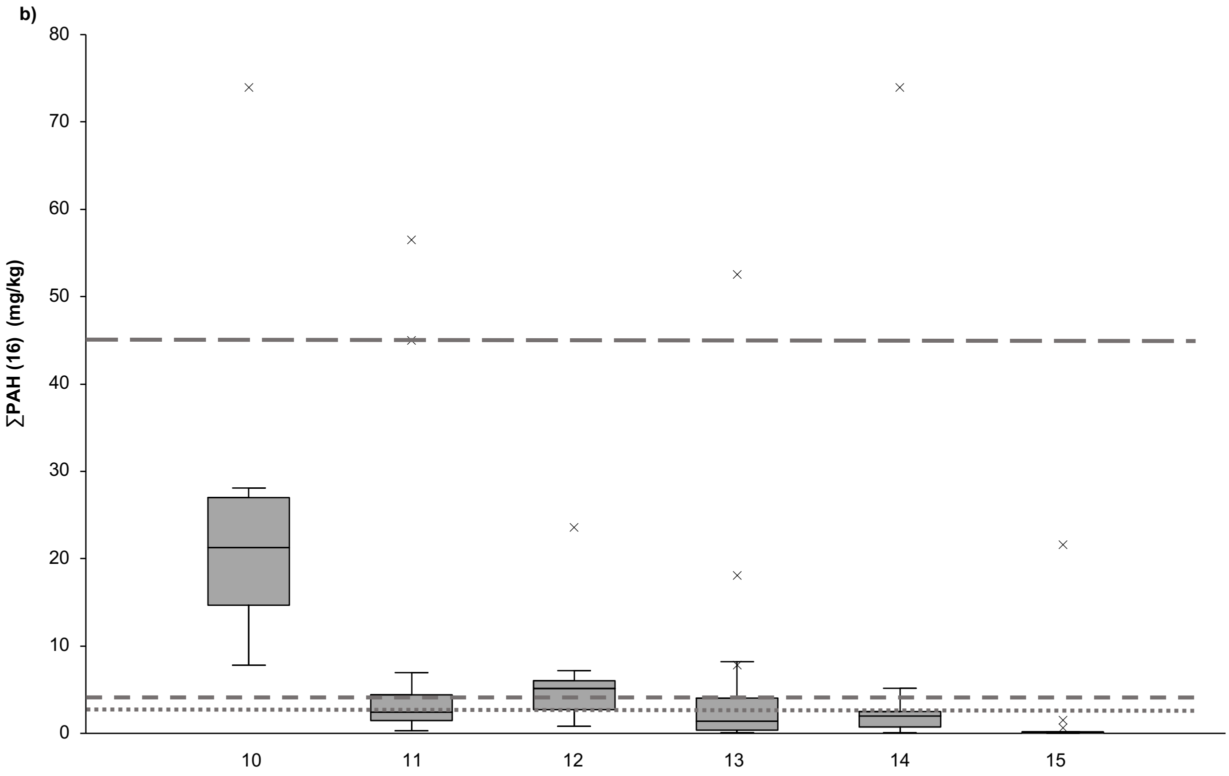
Benzo(a)anthracene	0.0748	176 (30.3)	2.50 (2.13)	0.693	65 (11.2)	3.94 (8.09)
Chrysene	0.108	178 (30.7)	1.98 (1.83)	0.846	70 (12.1)	3.38 (6.49)
Benzo(a)pyrene	0.0888	145 (25.0)	2.18 (2.08)	0.763	46 (7.9)	3.37 (5.90)
Dibenz(a,h) anthracene	0.00622	292 (50.3)	13.51 (41.63)	0.135	28 (4.8)	3.65 (4.59)

	NOAA Marine SQG					
	ERL			**ERM**		
$\sum\text{PAH}_{16}$	4.022	124 (21.4)	1.41 (1.61)	44.792	18 (3.1)	1.56 (2.10)

4.3.3 Distribution of $\sum\text{PAH}_{16}$ within SCHs

Figure 4.4 (a-c) shows the distribution of $\sum\text{PAH}_{16}$ concentrations among individual SCHs, organized by region. SQGs are included to aid in interpretation and outlier concentrations are noted with an asterisk (*). Six extreme outliers were omitted as they severely hindered plot design (mg/kg): Fig.4a: Baileys Brook (42.803), Pictou Landing (27.520), Skinners Cove (110.983), Fig.4b: Canso (336.770, 320.450), Fig.4c: Clarks Harbour (261.729).


a)
25
20
15
10
5
0
1
2
3
4
5
6
7
8
9


b)
∑PAH (16) (mg/kg)
80
70
60
50
40
30
20
10
0
10
11
12
13
14
15

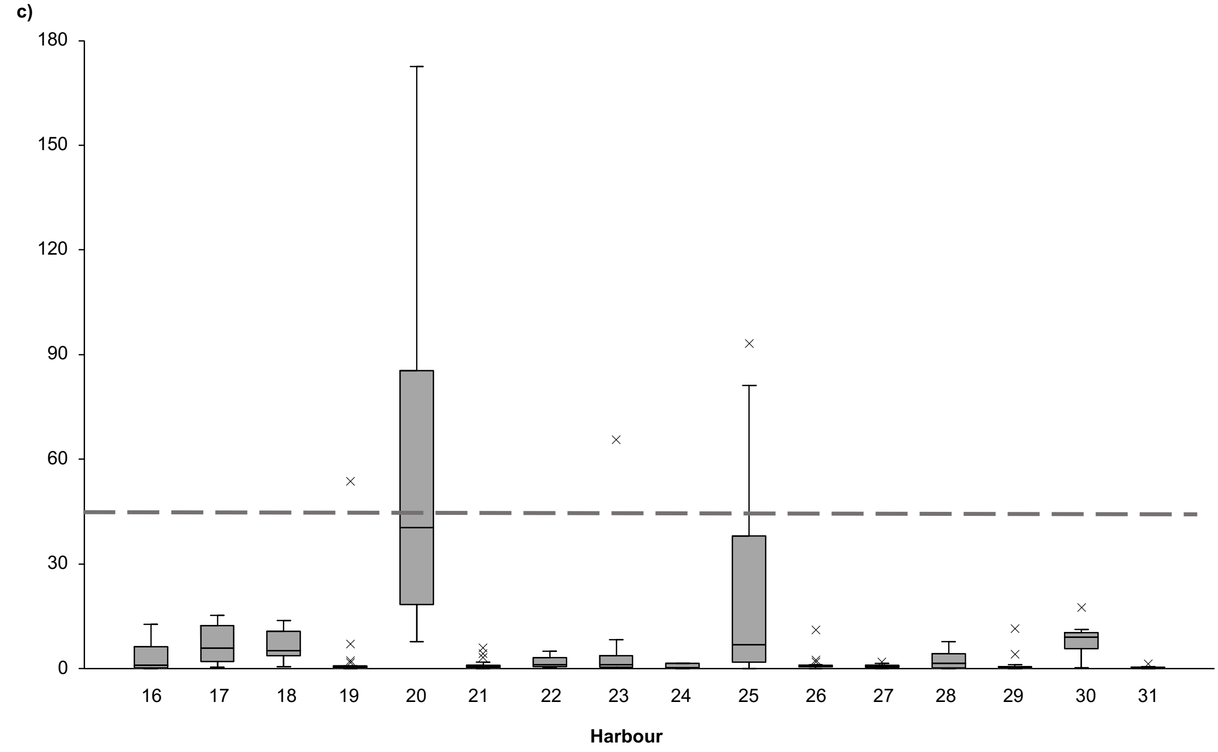

c)
180
150
120
90
60
30
0
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
Harbour

Figure 4.4 (a-c) Distribution of $\sum PAH_{16}$ concentrations among Gulf (a), Eastern (b), and Southwest (c) SCHs. Individual harbours are organized by their corresponding number (1-31). Outliers are noted with an (x). Select sediment quality guidelines (SQGs) are included as horizontal lines: smallest dashed line represents the CEPA Disposal at Sea Regulations guideline (2.5 mg/kg), medium dashed line represents the NOAA ERL (4.022 mg/kg) and the largest dashed line represents the NOAA ERM (44.792 mg/kg).

There is a high degree of variation among NS SCH $\sum PAH_{16}$ distributions. The majority of NS SCHs demonstrate narrow distributions, with many outliers both present and omitted. Fox Point (*n*=6), Moose Harbour (*n*=19), and Canso (*n*=12) demonstrate the widest variation of $\sum PAH_{16}$. The Gulf region demonstrates the lowest $\sum PAH_{16}$ distributions, as none exceed the ERM. All Eastern region SCH distributions are less than the ERM value, with the exception of outliers from Canso and Glace Bay. In the southwest, Fox Point and Moose Harbour distributions exceed the ERM, alongside outliers from Delaps Cove and Little Harbour Shelburne. This is an indication that harbours of the Gulf region are the least influenced by PAH contamination, while those of the Southwest region are the most influenced.

Box plot distributions provide insight to trends among sediment samples at each SCH. It can be inferred that the high mean $\sum PAH_{16}$ for Canso (77.576 mg/kg) (Fig. 4.2) is greatly influenced by omitted outliers, as the outlier-free box plot distribution does not exceed 30 mg/kg. In contrast, the Fox Point distribution shows that nearly 50% of $\sum PAH_{16}$ values fall above the ERM. This is an indication that many Fox Point samples provided high $\sum PAH_{16}$ concentrations and that the mean $\sum PAH_{16}$ of 62.120 mg/kg is not a function of outliers.

4.3.4 Mean $\sum PAH_{16}$ Comparison to Global Harbours

To contextualize $\sum PAH_{16}$ values of NS SCHs, a comparison was made to harbours around the world. Table 4.4 shows $\sum PAH_{16}$ for all 31 SCHs combined, alongside other harbours from Canada, US, Europe, Asia, and other locations. To determine the mean and range of $\sum PAH_{16}$ in this study, all samples (*n*=580) among all SCHs were combined to determine a representative value. Comparison to other global harbours was completed by assessing mean $\sum PAH_{16}$ and/or the range $\sum PAH_{16}$ among sediments. The PAH pollution level of each harbour site was estimated by comparing the $\sum PAH_{16}$ range to ERL and ERM benchmarks.

Table 4.4 Comparison of NS SCH sediment $\sum PAH_{16}$ to global harbours. PAH pollution level is estimated as low: <ERL, moderate: >ERL, <ERM, high: >ERM.

Location	$\sum PAH_{16}$ Range (mg kg^{-1})	$\sum PAH_{16}$ Mean (mg kg^{-1})	PAH Pollution Level	Reference
Canada				
31 Nova Scotia core fishing SCHs	0.037-336.770	6.007 (+/-25.686 SD)	Low- High	Present study
Halifax Harbour, NS	0.510-25.430	---	Low-Moderate	Tay et al. (1992)
Sydney Harbour, NS	1.400-73.800	---	Low-High	Walker et al. (2013a)
Saint John Harbour, NB	0.380-10.630	1.300	Low-Moderate	Zitko (1999)
Vancouver Harbour, BC	4.300-11.000	---	Moderate	Bolton et al. (2004)
United States				
Boston Harbour	7.266-358.092	---	Moderate- High	Wang et al. (2001)
Lavaca Bay (Texas)	0.0659-77.309	14.257	Low-High	Carr et al. (2001)
Mexico				
Todos Santos Bay	0.007-0.813	0.096	Low	Macías-Zamora et al. (2002)
Europe				
Norwegian Harbours (4), Norway	2-113	---	Low-High	Oen et al. (2006)
Lebanon				
Port of Tripoli	0.243-2.965	1.061	Low	Merhaby et al. (2015)
Asia				
Kaohsiung Harbor, Taiwan	0.472-16.201	5.764	Low-Moderate	Chen and Chen (2011)
Tokyo Bay, Japan	0.109-1.170	0.690	Low	Horii et al. (2009)

$\sum PAH_{16}$ concentrations for this study ranged from 0.037-336.770 mg/kg for all SCHs combined, with a mean $\sum PAH_{16}$ of 6.007 mg/kg. NS SCHs reflect wide variation of $\sum PAH_{16}$ concentrations which range from low to high risk for biota impairment. Mean $\sum PAH_{16}$ sediment concentrations for the present study exceeds the CEPA (1999) Disposal at Sea Regulations Guideline (2.5 mg/kg) and the ERL (4.022 mg/kg) yet falls below the ERM (44.972 mg/kg). This suggests that on average, $\sum PAH_{16}$ concentrations among the 31 SCHs may only occasionally impair biota.

Mean $\sum PAH_{16}$ sediment concentrations among NS SCHs most closely aligns with the mean $\sum PAH_{16}$ of Kaohsiung Harbour in Taiwan. Kaohsiung Harbour is the largest international port in Taiwan and exceeds the size of many NS SCHs. Kaohsiung Harbour is primarily a commercial site, with upwards of 30,000 container ships using this site every year. Kaohsiung Harbour has known pollution inputs that are amplified by four contaminated rivers that enter into the harbour and carry wastewater from multiple upstream sources. However, Kaohsiung Harbour is similar to NS SCHs as it supports the fisheries through multiple fishing port stations (Chen and Chen, 2011).

The majority of $\sum PAH_{16}$ sediment concentrations for the present study fall within ranges presented by Boston Harbour. Boston Harbour has been described as one the "most polluted harbours in the United States" (Wang et al., 2001), as very high PAH concentrations in sediments have been reported, suspected from industrial and municipal contamination inputs (Shiaris, 1989). This suggests that certain samples and/or individual SCHs demonstrate $\sum PAH_{16}$ concentrations which mimic a heavily polluted harbour site.

In the Canadian context, the $\sum PAH_{16}$ range among NS SCHs is higher than other Canadian harbours, including Vancouver (BC), Halifax (NS), and Sydney (NS). These harbours (Vancouver, Halifax, and Sydney) are very different as compared to NS SCHs. Vancouver and Halifax harbours are the two largest ports on the western and eastern coasts of Canada, respectively, and both primarily serve commercialized purposes (Levings et al., 2004; Robinson et al., 2009; Walker, 2016). Sydney Harbour in Cape Breton, NS, is historically an industrial harbour that has been subjected to legacy contamination issues given neighbouring industrial activities for decades (Walker et al., 2015a). The purpose of NS SCHs differs greatly from other harbours included in Table 4.4. The majority of SCHs are home to small fishing vessels that support inshore fisheries, including lobster, and often employ vessels which are approximately 14 m in length (DFO, 2018c). SCHs do not play a large role in commercialization and therefore do not support large vessel traffic. Similarly, SCHs are often not plagued with historical contamination issues, unlike larger global sites.

Large variation in range of $\sum PAH_{16}$ sediment concentrations among NS SCHs can be partly explained by data collection methods used to derive $\sum PAH_{16}$ mean and range. For example, sediments were collected using different sampling techniques (grabs *vs.* cores, composite *vs.* discrete). Values were derived from a large sample dataset (*n*=580), over a long temporal period (17 years), across many independent SCH sites (*n*=31). Subsequently, these spatial and temporal characteristics could encourage a large amount of variation for $\sum PAH_{16}$ concentrations. This is also supported by Fig. 4.2 and Fig. 4.3 in that the $\sum PAH_{16}$ range is likely varied due to high $\sum PAH_{16}$ of a select few SCHs (Canso, Fox Point, Moose Harbour). Dredging on a regular basis may also be a contributor to variation in grain size distributions and other physicochemical characteristics of SCHs and lend itself to a high degree of variation in contaminant concentrations among SCHs (Chen et al., 2012).

4.3.5 Relative Abundance: PAH_{16} Profile Distribution

Relative abundance (RA), shows how individual compounds contribute (on a mg/kg dry weight basis) to total PAH concentration among all samples within a region. The equation used to determine relative abundance uses the concentration values of mg/kg and then determines the RA of a compound on a percent (%) basis, reflecting an average RA value for each compound within samples of each region independently (Eq 1):

$$RA= \left(\frac{\text{Summation of Concentration of Compound (x)}}{\text{Summation} \sum \text{PAH16}}\right) * 100 \qquad \text{(Eq 1)}$$

The RA distribution of 16 PAH compounds for the Gulf, Eastern, and Southwest regions is presented in Fig. 4.5. The distribution of RAs among the 16 PAH compounds follows a similar distribution for the Gulf, Eastern, and Southwest regions. The highest RA values are represented by high molecular weight PAHs (compounds contain >3 aromatic rings) including fluoranthene, pyrene, and chrysene. The abundance of high molecular weight PAHs in sediment profiles is a trend that has been observed globally (McCready et al., 2000; Stout et al., 2004).

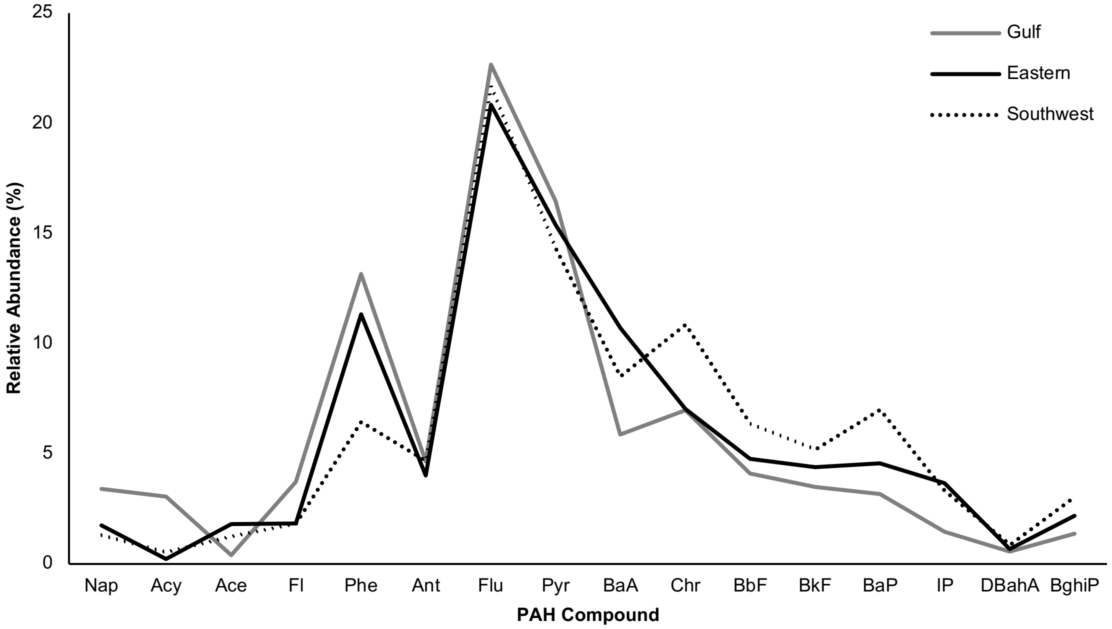


Figure 4.5 Distribution of individual PAHs (EPA 16) across Gulf, Eastern, and Southwest regions, reflected as relative abundance (%). Relative abundance values for each compound are a function of the total concentration of the compound relative to all samples within each respective region.

From an environmental management perspective, the similarities in PAH (16) distribution profiles between regions suggests that PAHs are likely from similar sources (McCready et al., 2000). Given that regions have different physicochemical characteristics (grain size, TOC, TIC), this suggests that post-depositional processes (including photolysis, biodegradation) may not be a significant consideration when addressing PAHs in SCHs across NS (McCready et al., 2000; Marr et al., 2006).

4.3.6 Relative Abundance: Individual PAHs

NS SCH sediments are dominated by six individual PAH compounds: fluoranthene (Flu), pyrene (Pyr), phenanthrene (Phe), chrysene (Chr), benzo(a)anthracene (BaA) and benzo(b+k) fluoranthene [B(b+k)F] (Fig. 4.6). RA sums of these six compounds together contribute over 70% to the entire sampling sets within each region. The remaining contributions (%) for each region are distributed among 11 other PAH compounds. Flu represents the greatest contributor consistently among regions, with RA abundance values of 22.7, 21.7, and 20.8% for the Gulf, Southwest and Eastern regions, respectively. Pyrene represents the second greatest contributor consistently among regions, with RA values of 16.5, 14.3 and 15.4% for the Gulf, Southwest and Eastern regions, respectively.

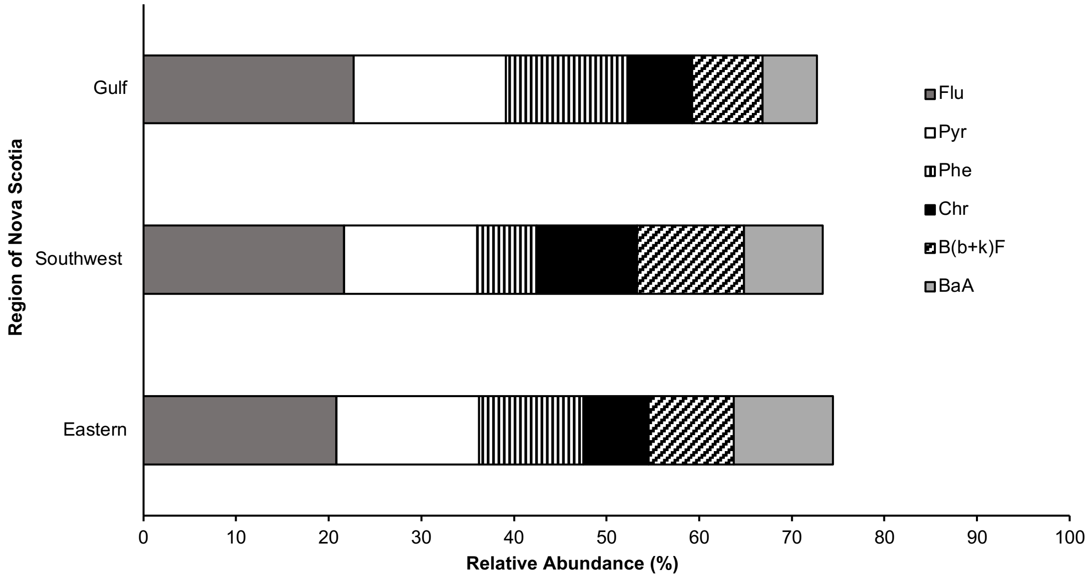


Figure 4.6 Contributions (%) of the six most abundant PAHs in sediments among regions of Nova Scotia, as reflected by their relative abundance to all other PAHs in samples within each region. Abbreviations include: fluoranthene (Flu), pyrene (Pyr), phenanthrene (Phe), chrysene (Chr), benzo(b+k)fluoranthene (B(b+k)F), and benzo(a)anthracene (BaA).

Both Flu and Pyr are strongly associated with urban background sources of PAHs, and their abundance in NS SCH sediments may provide insight to dominating PAH sources (Stout and Graan, 2010). The six largest contributing compounds are all considered high molecular weight PAHs, with the exception of (Phe) which is considered a low molecular weight PAH. Zitko (1999) identified a similar trend in sediments retrieved from the Saint John river in New Brunswick, Canada, from 1996-1999. Zitko (1999) determined that abundance of species followed the following trend of greatest abundance to lowest abundance: Flu, Pyr, Phe, B(b+k)F, Chr, BaA. In the Saint John sediments, Flu, Pyr, and

Phe contributed nearly 40% to the total PAH amount, while all six compounds listed above would form around 70% of the total PAH. As demonstrated in Fig. 6, the distribution trend holds true for NS SCHs.

These results align with the mean, standard deviation of the mean, range, and median presented for all samples combined (*n*=580) for the 19 PAHs typically assessed in MSSPs (Table 4.5). The six most highly abundant PAHs [Flu, Pyr, B(b+k)F, Phe, Chr, and BaA] demonstrate the highest mean concentrations across all PAHs. Flu and Phe present the highest maximum values among concentrations, with 100 and 76 mg/kg, respectively. Similar results have been identified widely in the literature (Zitko, 1999; McCready et al., 2000; Bolton et al., 2004). Bolton et al. (2004) noticed similar trends in sediments retrieved from Vancouver Harbour, Canada, in that high molecular weight PAHs demonstrated higher concentrations as compared to lower weight PAHs. Guo et al. (2006) suggest that the stability and abundance of high molecular weight PAHs make them very helpful in assessing PAH contribution sources.

Table 4.5 Summary of 19 individual PAH concentrations in NS SCH sediments (2001-2017). PAHs presented (*n*=19) are those which are typically assessed as part of MSSPs/ESAs. Low molecular weight PAHs are classified as those with 3 aromatic rings or less, while high molecular weight PAHs contain >3 aromatic rings).

Parameter	Molecular Weight	Mean (mg/kg)	Standard Deviation	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)
Naphthalene	Low	0.1131	0.8493	0.0070	0.0025	13.0
1-Methylnaphthalene	Low	0.0541	0.2753	0.0025	0.0025	3.6
2-Methylnaphthalene	Low	0.0791	0.4583	0.0070	0.0025	6.8
Acenaphthylene	Low	0.0248	0.1693	0.0025	0.0020	4.0
Acenaphthene	Low	0.1113	0.8162	0.0120	0.0020	15.0
Fluorene	Low	0.1337	0.7497	0.0200	0.0025	12.0
Phenanthrene	Low	0.5908	3.7046	0.0500	0.0025	76.0
Anthracene	Low	0.2810	1.2930	0.0250	0.0000	21.0
Fluoranthene	High	1.3678	6.7629	0.1700	0.0015	100.0
Pyrene	High	0.9572	4.5694	0.1100	0.0010	70.0
Benzo(a)anthracene	High	0.4768	2.1452	0.0460	0.0025	28.0
Benzo(k)fluoranthene	High	0.2955	1.2835	0.0250	0.0025	18.0
Benzo(b)fluoranthene	High	0.3509	1.3958	0.0360	0.0020	18.0
Chrysene	High	0.5622	2.2318	0.0685	0.0025	27.0

Parameter	Molecular Weight	Mean (mg/kg)	Standard Deviation	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)
Benzo(a)pyrene	High	0.3504	1.5373	0.0300	0.0015	21.0
Perylene	High	0.1252	0.4806	0.0250	0.0025	6.5
Indeno(1,2,3-cd)pyrene	High	0.1712	0.7563	0.0250	0.0020	9.2
Dibenz(a,h)anthracene	High	0.0468	0.1887	0.0075	0.0015	2.4
Benzo(ghi)perylene	High	0.1571	0.6611	0.0250	0.0020	8.6

4.3.7 Individual PAHs: SQG Comparison

The CCME has outlined ISQG and PEL guideline values for the protection of aquatic life for 13 individual PAHs in marine sediments. Compounds were compared to ISQG and PEL values as an average of all combined samples (*n*=580), across all SCHs to determine the frequency of exceedances (Table 4.3). It does not come as a surprise that PAHs in NS SCHs exceed ISQGs more frequently than PELs, as ISQGs are more conservative SQGs. Of the 13 PAHs, Dibenzo (a,h)anthracene (DbahA) exceeded ISQGs most frequently among samples (50.3%) and demonstrates the highest degree of difference among samples. Degree of difference calculations are an indication to how much a sample exceeds a guideline, relative to the guideline itself. A high degree of difference can be interpreted by two separate, but connected, ideas. The first, is that a high degree of difference simply indicates and explains that compounds are present in very large concentrations relative to the guideline. In contrast, it can also be an indication that the guideline used is extremely conservative. As guidelines are derived in different ways, their level of conservatism can vary (Chapman and Mann, 1999; Birch, 2018). Guidelines which are conservative may have a higher likelihood of suggesting sediment toxicity when sediments are in fact clean and an example of this is that CCME ISQGs are more conservative than their PEL counterparts, as they represent lower-level guidelines. On average, the degree of difference between DbahA concentrations in samples and the ISQG was 13.51 times the ISQG value (13.51 x 0.00622). The CCME ISQG value for DbahA is the second lowest ISQG for all 13 PAHs and the high degree of difference value may be an indication that this value may be too conservative for this compound in NS SCHs. This calculation supports the use of PEL guideline values as they can provide a stronger indication of biological impairment and are less likely to suggest sediment toxicity as compared to ISQGs. Naphthalene (Nap) demonstrated the lowest percent of ISQG and PEL exceedances (13.8 and 2.6%, respectively). Anthracene (Ant) demonstrated the highest frequency of PEL exceedances (16%), while the greatest degree of difference among compounds for PELs was Acenaphthene, at 12.90 times the PEL. On average, high molecular weight PAHs demonstrate a slightly greater frequency of exceedance as compared to low molecular weight PAHs, for both ISQG (1249 for HMW, 1222 for LMW) and PELs (354 for HMW, 334 for LMW). This supports the notion that high molecular weight PAHs are more likely to exceed CCME guidelines in NS SCH sediments, suggesting that they may present a greater risk to biota, as compared to low molecular weight PAHs.

4.4 CONCLUSION

The majority of selected SCHs exhibit sediment total PAH concentrations which do not pose a high risk to biota and fall below recognized SQGs. Results suggest that sediments of the Gulf region are the least contaminated by PAHs, while the Southwest appears to be most contaminated. Most SCHs exhibit sediment PAH concentrations which are unlikely to impair biota. However, Canso and Fox Point in the Southwest exhibit elevated concentrations of PAHs, that suggest frequent impairment to biota. Therefore, results suggest that these two SCHs should be prioritized by federal custodians for further assessment and delineation of PAHs. US EPA 16 PAHs are distributed (in abundance) similarly across the regions of NS, indicating that PAH input sources may be similar among regions, and that the physicochemical characteristic differences (TOC, grain size) among regions may not greatly influence PAH distributions. High molecular weight PAHs, especially Flu and Pyr, show the highest concentrations among samples, which aligns widely with trends from the greater literature. Further assessment of physicochemical characteristics of sediments and temporal trends across regions of NS would further contribute and support a comprehensive analysis of PAHs in NS SCHs.

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CHAPTER 5
SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SMALL CRAFT HARBOUR (SCH) SURFICIAL SEDIMENTS IN NOVA SCOTIA, CANADA*

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Abstract: Multiple source apportionment approaches were employed to investigate and identify PAH sources of which contribute to small craft harbour (SCH) sediments in Nova Scotia (NS), Canada. A total of 580 sediment samples were analyzed using PAH diagnostic ratios, Unmix Optimum receptor modelling, and by assessment of the composition of the PAH profile. PAH diagnostic ratios suggest PAHs are primarily of pyrogenic origin, while Unmix receptor modelling identifies four individual sources which best describe surficial sediments and suggest contributions from both pyrogenic and petrogenic origins. These include coal combustion, automobile exhaust, and biomass incineration. PAH profile compositional assessment determined an overwhelming contribution of high molecular weight PAHs (4-6 aromatic rings), suggesting PAHs are of pyrogenic origin, and exhibiting strong correlation with the total PAH concentration of samples. Surficial sediments in NS SCHs exhibit PAH source signatures which appear to be a mixture of both localized and potential long-range PAH sources.

Key words: Polycyclic aromatic hydrocarbons (PAHs); Small craft harbour (SCH) sediments; Source apportionment; Multivariate Receptor Modelling; Unmix Optimum; PAH diagnostic ratios; Biomass; Coal; Vehicular Emissions; Nova Scotia

** Prepared as an article for Science of the Total Environment*

5.1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are pollutants observed in aquatic, terrestrial, and atmospheric environments around the world. PAHs are considered priority pollutants as they may demonstrate carcinogenic and mutagenic attributes and have been shown to have subsequent adverse effects on aquatic organisms in a wide range of studies (Yunker et al., 2002; Fang et al., 2012; Stout et al., 2015). PAHs are introduced into the environment from a variety of sources including pyrogenic, petrogenic, and natural sources (Lima et al., 2005; Jiang et al., 2009). Pyrogenic PAH sources are characterized by high temperature combustion of fossil fuels or organic matter, which often release PAHs into the atmosphere through exhaust and soot (Masood et al., 2016). PAHs released from high temperature processes tend to be of high molecular weight (HMW) and have increased persistence in the environment (4-6 aromatic rings) (Hwang et al., 2003; Smith et al., 2009; Mostert et al., 2010). PAHs of petrogenic origin are formed from petroleum (crude and refined) and enter the environment by spills, petroleum combustion, discharges, and terrestrial run off (Masood et al., 2016). These PAHs (produced by lower temperature processes) tend to be of lower molecular weight (LMW) (2-3 aromatic rings) (Hwang et al., 2003; Mostert et al., 2010). PAHs can be naturally produced by forest fires and diagenesis (Wang et al., 2007; Mahanty et al., 2011). PAHs primarily enter the environment by initial release into the atmosphere from incomplete combustion processes and then subsequently enter into soil, sediments, and water bodies from fluvial and atmospheric transport processes (Doong and Lin, 2004; Stout and Emsbo-Mattingly, 2008). The anthropogenic reliance on and historical use of fossil fuels has contributed to PAHs in the environment globally. The presence of PAHs derived from primarily from pyrogenic sources is often referred to as "urban background" (Hoffman et al., 1984; Stout et al., 2004; Zemo, 2009).

From an ecological risk perspective, PAH sources are of concern as PAHs from different sources can impact biota differently. In aquatic environments, petrogenic PAHs may be more readily available for bio-accumulation by aquatic species as compared to pyrogenic PAHs (Thorsen et al., 2004). Pyrogenic PAHs, which are characterized by HMW, are often less available in the aquatic environment given their ability to settle more rapidly (as compared to LMW PAHs) into the sediment fraction of the water column and sorb to sediment particles (Koelmans et al., 2006; Chen and Chen, 2011).

As PAHs enter the environmental from a variety of different sources, source apportionment of PAHs is of importance for environmental management and has been well studied over the last 40 years (Tobiszewski and Namieśnik, 2012; Nádudvari et al., 2018). Source apportionment research began in the 1970s, with researchers conducting both local and global studies aiming to characterize PAH sources in the environment by analysis of PAH compositions and concentration levels (Blumer and Youngblood, 1975; Youngblood and Blumer, 1975; Lee et al., 1977; Laflamme and Hites, 1978). Similarly, varying levels of alkylation of PAHs helped scientists to better understand the sources of PAH compounds with new analytical methods during this time (Wise et al., 2015; Stout et al., 2015). Since then, many studies have investigated PAHs in environments around the world (Killops and Massoud, 1992; McCready et al., 2000; Jiang et al., 2009; Chen and Chen, 2011; Van Metre and Mahler, 2014; MacAskill et al., 2016). Source apportionment of PAHs (and other environmental pollutants) continues to progress with the rise of environmental forensic methodologies and advancements in technology (Lima et al., 2005; Walker et al., 2017; Nádudvari et al., 2018).

There are many forensic methodologies that can aid in determining source contributions and source identification of PAHs. However, methodologies should be carefully applied with the weaknesses, assumptions, and uncertainty of the methodology in mind. To account for this, employing multiple source apportionment methods may strengthen source apportionment estimations by providing corroborative evidence (Stout and Graan, 2010). To date, a spatially summarized analysis of PAH source apportionment has yet to be completed for surficial sediments in Nova Scotia (NS). Therefore, this study aims to characterize PAH sources from sediments collected from 31 NS small craft harbours (SCHs) between 2001-2017, by implementing multiple lines of evidence. The three lines of evidence used in support of this investigation include: PAH diagnostic ratios, Unmix Optimum receptor modelling, and PAH profile composition assessment. This study aims to support SCH management in NS by providing harbour decision makers with information that supports the maintenance and prioritization of SCH sites, particularly in regard to source control of contaminants. Similarly, this study builds on earlier PAH characterization completed at these SCHs (Davis et al., 2018).

5.1.1 PAH Compounds

The 16 PAH compounds assessed as part of this study are those which are classified as priority pollutants by the United States Environmental Protection Agency (US EPA, 2014). These PAHs are considered “parent” PAHs, as they lack alkyl group(s) (a fragment of carbon and hydrogen atoms) and are considered non-substituted (Zemo, 2009; Tobiszewski and Namieśnik, 2012). Many other PAH compounds, of which are alkylated (substituted), are known to occur in the environment, yet the 16 parent PAH compounds are the focus of this study given their priority status by the EPA and that they are most frequently measured in the environment (Zemo, 2009). The 16 PAHs, alongside their molecular weight and atomic ring characteristics are outlined in Table 5.1.

Table 5.1 Chemical characteristics of PAH species assessed in current study.

Chemical name	**Abbreviation**	**Mass (g mol^{-1})**	**Atomic Rings**
Naphthalene	Nap	128	2
Acenaphthylene	Acy	152	3
Acenaphthene	Ace	154	3
Fluorene	Fl	166	3
Anthracene	Ant	178	3
Phenanthrene	Phe	178	3
Fluoranthene	Flu	202	4
Pyrene	Pyr	202	4
Benzo(a)anthracene	BaA	228	4
Chrysene	Chr	228	4
Benzo(b)fluoranthene	BbF	252	5
Benzo(k)fluoranthene	BkF	252	5
Benzo(a)pyrene	BaP	252	5
Dibenzo(a,h)anthracene	DBahA	278	5
Benzo(g,h,i) perylene	BghiP	276	6
Indeno(1,2,3-cd)pyrene	IP	276	6

5.1.2 PAH Species Classification

PAHs can be grouped based on the number of atomic rings they contain. The number of atomic rings is a feature that is useful in attempting to apportion PAH sources, as individual PAHs and groups of PAHs of the same atomic ring classification may be characteristic of specific source(s). Certain PAHs may originate or be tracers/markers for a variety of different sources. The US EPA priority 16 PAHs are often produced from a variety of sources, of which are summarized below.

- **Two ring PAHs:** Naphthalene is the only US EPA priority 16 PAH species that contains two atomic rings. Naphthalene naturally occurs from coal tar, soot and pitch, and can originate from crude oil (Iglesias et al., 2002). Naphthalene is found in high proportions in coal tar (Ghoshal et al., 1996). Creosote (a historical wood preservative) is high in naphthalene (Ye et al., 2016).

- **Three ring PAHs:** Acenaphthylene, acenaphthene, fluorene, anthracene, and phenanthrene are US EPA priority 16 PAHs that contain three atomic rings. These compounds are found naturally within fossil fuels (coal, coal tar, crude oil), and also originate from the incomplete combustion of coal, biomass, and other fossil fuel derivatives (Duval and Friedlander, 1981; Ravindra et al., 2008; Achten and Hoffman, 2009; Nádudvari et al., 2018). Achten and Hoffman (2009) suggest that fluorene and phenanthrene show high proportions within coal. Diesel emissions also produce compounds of this classification (Yang et al., 1998, Caricchia et al., 1999; Ho et al., 2002; Omar et al., 2002; Fang et al., 2004; Ravindra et al., 2006 a,b). Ravindra et al. (2008) suggest that acenaphthylene, acenaphthene, and anthracene are tracer compounds for cement plant emissions. Similarly, phenanthrene and anthracene can be indicators of biomass burning, coal combustion, and coke production processes (Duval and Friedlander, 1981, Harrison et al., 1996).

- **Four ring PAHs:** Fluoranthene, pyrene, benzo(a)anthracene, and chrysene are US EPA priority 16 PAHs that contain four atomic rings. Four ring PAH species occur naturally in coal, coal tar, and in crude oil (Oros and Simoneit, 2000; Li et al., 2012; Grafka et al., 2015; Nádudvari et al., 2018). From an anthropogenic perspective, these compounds may originate from various incineration processes (domestic burning or industrial burning of waste/coal) (Simoneit et al., 2005; Ravindra et al., 2006a) and pyrene tends to be a strong tracer compound for incineration (Duval and Friedlander, 1981). Fluoranthene, pyrene, benzo(a)anthracene, and chrysene are also suggested tracer compounds for coal combustion (Duval and Friedlander, 1981).

- **Five ring PAHs:** Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and dibenzo(a,h) anthracene are US EPA priority 16 PAHs that contain five atomic rings. In the past, coal combustion was suggested as the source responsible for the majority of BaP, yet this has become less of a dominating source over time (Commins and Hampton, 1976). Benzo(b)fluoranthene and benzo(k)fluoranthene are characteristic of diesel-specific vehicle emissions (Duval and Friedlander, 1981).

- **Six ring PAHs:** Benzo(g,h,i) perylene, and indeno(1,2,3-cd) pyrene are US EPA priority 16 PAHs that contain six atomic rings. BghiP is strongly considered a tracer compound for vehicle traffic emissions (Duval and Friedlander, 1981), while Guo et al (2003) suggest that both BghiP and IP are tracer compounds for gasoline vehicle emissions. BghiP may also be a tracer compound for coke production (Duval and Friedlander, 1981).

5.2 MATERIALS AND METHODS

5.2.1 Study Area

Sediments assessed as part of this study were retrieved from 31 SCHs across the coastal province of NS, Canada. The 31 SCHs were distributed across the Gulf (*n=9*), Eastern (*n=6*), and Southwest (*n=16*) management regions in NS, as defined by the Department of Fisheries and Oceans (DFO). The spatial distribution of these SCHs is outlined in Figure 5.1.

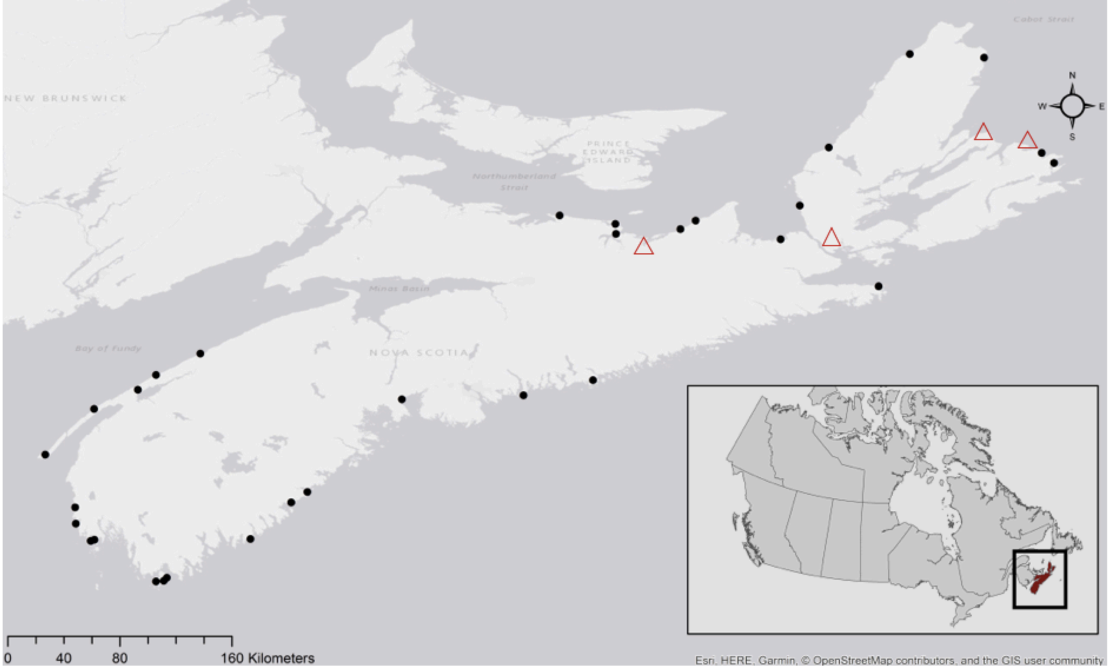


Figure 5.1 Spatial distribution of selected 31 small craft harbour sites across Nova Scotia, Canada. Harbours are represented as black dots, and red triangles represent the approximate locations of four Nova Scotia Power coal and/or pet coke power generation stations [Adapted from Davis et al. (2018)].

5.2.2 Sediment Data

PAH information was assessed by secondary analysis of historical sediment data for 31 individual SCHs. Individual PAH compounds which were of focus in this study are detailed in Table 5.1. Sediment data was given by the Canadian federal government (Fisheries and Oceans Canada-Small Craft Harbour (DFO-SCH) Branch and Public Services and Procurement Canada (PSPC)) and encompassed federally mandated sediment sampling reports between the years 2001-2017. Surficial sediment sampling (0-10 cm) was primarily conducted as part of the federal Marine Sediment Sampling

Program prior to dredging activities at all sites. The term “sediment” will refer to sediment samples collected at the depth of 0-10 cm throughout this study. The 31 SCH sites were sampled at varying intervals during the temporal period. The majority of samples included surficial sediments and all samples were analyzed by Standards Council of Canada accredited commercial laboratories. SCHs in this study (*n*=31) are classified as core fishing harbours by DFO-SCH. Further details regarding SCH selection, geographical location of specific SCHs, and the physicochemical characteristics of sediments analyzed is outlined in previous work by Davis et al. (2018).

5.2.3 PAH Diagnostic Ratios

PAH diagnostic ratios are an extremely common source apportionment approach to PAHs, and seek to understand PAH sources through two main concepts (Tobiszewski and Namieśnik, 2012):

- PAHs always enter the environment as mixtures
- Molecular proportions of PAH species can provide insight to PAH sources

PAH diagnostic ratios are often applied by pairing isomeric pairs (e.g., PAH species with the same chemical formula; e.g., phenanthrene and anthracene; fluoranthene and pyrene; chrysene and benzo(a)anthracene; benzo(g,h,i) perylene and indeno (1,2,3-cd) pyrene) (Yunker et al., 2002; Tobiszewski and Namieśnik, 2012; Wise et al., 2015). Sourcing can be inferred from the change in the amount of the less stable (kinetic) PAH in comparison to the more stable PAH (thermodynamic) in the isomeric pair (Yunker et al., 2002; Yunker et al., 2011). As an example, in the diagnostic ratio pairing of Anthracene/(Anthracene+Phenathrene), (Ant) is more kinetic than its paired compound (Phe) (Yunker et al., 1996). A low ratio from this pair indicates a higher amount of thermodynamic phenanthrene and suggests petrogenic origin. In contrast, a higher ratio would indicate a larger amount of kinetic anthracene, which indicates combustion origins (Yunker et al., 1996; Yunker et al., 2002).

PAH diagnostic ratios are useful in coarsely distinguishing between pyrogenic and petrogenic sources of PAHs, but their application can be limited in further distinguishing between different pyrogenic or petrogenic sources because of the potential for overlap among ratio ranges (Yunker et al., 2002; Stout et al., 2004). Caution should be applied in using diagnostic ratios because of the similarities observed between sources, especially those which are pyrogenic (Galarneau, 2008). The following diagnostic ratios were applied and interpreted by transitional values (values which indicate possible sources) from the greater literature:

- Mass 178: Anthracene/(Anthracene + Phenanthrene)
- Mass 202: Fluoranthene/(Fluoranthene+Pyrene)
- Mass 228: Benzo(a)anthracene/(Benzo(a)anthracene + Chrysene)
- Mass 276: Indeno(1,2,3-cd) pyrene/(Indeno(1,2,3-cd) pyrene +Benzo(g,h,i) perylene)
- ∑LMW/∑HMW PAHs

The ratio of ∑4 ring /∑5+6 ring PAHs was also applied to provide insight to the impact of localized or long-range transport processes. In application of PAH diagnostic ratios, only samples which demonstrated detectable concentrations of the PAHs were included. All samples which demonstrated concentrations below detection limits for one or both of the compounds included in the ratio were excluded.

5.2.4 Receptor Modelling

Source apportionment for environmental contaminants follows one of two over-arching approaches: source-oriented or receptor modelling approaches. Source oriented approaches apportion contaminants by understanding emission contributions and the processes pollutants undergo to arrive at a receptor (Hopke, 2016). In contrast, receptor modelling approaches focus on the contaminant profile of a receptor and from this, aim to understand the sources contributing to the receptor profile (Hopke, 2016; Sofowote et al., 2008; Hopke and Cohen, 2011). Conservation of mass and mass balance are important concepts in receptor modelling approaches, as they underlie the principle that species of compounds in a given sample are understood to have come from individual sources (Hopke and Cohen, 2011; Hopke, 2000). The detailed theory and application of receptor modelling in the environmental context are described in detail by Henry et al. (1984), Henry (1997; 2003), and Hopke (1985; 2016). Receptor modelling approaches include positive matrix factorization (PMF), chemical mass balance (CMB), multiple linear regression (MLR), and Unmix (Song et al., 2008; Feng et al., 2016). CMB, PMF, and Unmix have been well utilized by the United States Environmental Protection Agency (US EPA), as all three models have software available from the US EPA website for public use (Henry and Christensen, 2010).

5.2.4.1 Unmix Modelling

Unmix is a multivariate receptor modelling tool that was developed by the US EPA and determines source apportionment of contaminants by factor analysis. Specifically, Unmix uses principal component analysis (PCA) to reduce the dimensions of the data and identify factors (also known as sources) which best fit the data (Henry, 2003; Watson et al., 2008). Unmix looks for all of the possible edges produced from the data and uses the identification of an edge (hyperplane) to suggest a contribution from factors identified from the model algorithm (Henry, 1997, 2003; Watson et al., 2008). Unmix can be used without previous understanding of the specific sources impacting the data (Larsen and Baker, 2003).

5.2.4.2 Unmix Optimum Modelling

Unmix Optimum (Unmix O) is an advanced application of Unmix. Unmix O seeks to identify sources by using constrained non-linear optimization algorithms to refine the area (or volume) formed by vertices (factors). Unmix O was applied to the NS SCH sediment data set by use of an optimized interior point algorithm, as this algorithm is best suited for large data sets. A loose tolerance level (constraint level 1.1) was used to allow for negative source contributions. This encouraged the model to find an initial solution, while considering that Unmix O and Unmix models obey non-negativity constraints. An error level of 15% was used in this model application by a Monte Carlo method (Timmerman et al., 2007).

A total number of 509 observations were used in the model, with 14 individual PAHs included as variables. The 14 species were: acenaphthene (Ace), anthracene (Ant), Benzo(a) anthracene (BaA), benzo(a)pyrene, benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(ghi)perylene (BghiP), chrysene (Chr), fluoranthene (Flu), fluorene (Fl), indeno(1,2,3-cd) pyrene (IP), phenanthrene (Phe), pyrene (Pyr). 1 and 2- methylnaphthalene (1-MN and 2-MN) and perylene (Per) were excluded from the model due to a high number of missing data points among samples. Acenaphthylene (Acy), dibenz(ah)anthracene (DbahA) and naphthalene (Nap) were excluded as they provided outliers that degraded the fit of the model.

Sources identified by the Unmix model were further investigated by the following approaches:

- Consideration of fractional and percent source composition of individual PAHs within Unmix sources as compared to the literature (Table 5.2).
- The calculation of the normalized square difference and Chi^2 sum of each Unmix source as a comparison to 22 source profiles from the literature. This calculation compares the similarity of values between the source and a source profile from the literature. A lower calculated sum indicates increased similarity between compared profiles.
- PAH diagnostic ratio plots were used to compare Unmix sources to the 22 source profiles from the literature on the basis of individual single PAH isomer pairings (e.g., Flu:Pyr, BaA:Chr, Ant:Phe, IP:BghiP).

5.2.5 PAH Profile Composition Assessment

Sediments were assessed by reviewing the proportions of PAHs within samples that are present as part of the entire PAH profile. The PAH profile represents the collective PAHs assessed in NS SCH sediments (19 PAHs are typically assessed). Specifically, by organizing the PAH profile into defining characteristics, this approach can support source apportionment estimations as different individual PAHs, or groups of PAHs (e.g., 4-ring PAHs), can suggest an emission source(s). The number of atomic rings, molecular weight, classification of low molecular weight (LMW) or high molecular weight (HMW), and whether a PAH is deemed to be associated with “combustion” processes are all examples of PAH defining characteristics that can support source apportionment estimations. The number of atomic rings a PAH possesses, and whether a PAH is associated with a combustion source, are the two characteristics assessed in this study.

Samples were summarized within the regions of NS (Gulf, Eastern, Southwest) to determine the distribution of PAHs, as per their number of atomic rings. Raw PAH concentration data was used to calculate the total weight (mg/kg dry weight) of each atomic ring category (2-6 rings). The proportion of PAHs in each atomic ring category were calculated as a percent of the total PAHs present across all samples in the region. US EPA 16 priority PAHs were assessed and categorized. The calculated total PAH value for each region included 1-MN, 2-MN, and Per, of which were excluded from the atomic ring classifications. These compounds were included in the total PAH calculation because they were frequently measured as part of the analytical profile of the samples.

Similarly, the concentration of known combustion PAHs (∑Comb PAHs) was calculated by summing the amount of [Flu, Pyr, BaA, BbF, BkF, BaP, DBahA, BghiP] in all individual samples (across all 31 harbours). To investigate the relationship between ∑Comb PAHs and $\sum\text{PAH}_{16}$ Pearson correlation analysis was completed in Minitab Statistical Software® (Minitab Inc, State College, PA, 2010). In accompaniment to the above approaches, individual PAHs were assessed through comparison to the greater literature in support of source apportionment.

5.3 RESULTS AND DISCUSSION

5.3.1 Source Apportionment Using PAH Diagnostic Ratios

Four double PAH diagnostic ratios were applied to distinguish between pyrogenic and petrogenic origins of PAHs in NS sediments. Ranges used to interpret ratio values were derived from the expansive study completed by Yunker et al. (2002) in the Fraser River region of British Columbia, Canada, and from research completed by Dickhut et al. (2000) in Chesapeake Bay, US.

The Flu/(Flu+Pyr) ratio provides insight to petroleum, petroleum combustion, and combustion sources. Ratio values <0.4 indicate petrogenic sourcing, values between 0.4-0.5 are indicative of petroleum combustion, while values >0.5 suggest wood, grass, and/or coal combustion. In application of this ratio, an overwhelming grass, wood and coal combustion signature was identified, as all regions and the combined sediments reflected mean ratio values which fell above the combustion transition value of 0.5 (Fig 5.2). Mean ratio values among regions ranged between 0.57-0.59. This range of values aligns closely with the regional ratio values determined by Yunker et al. (2002) in the Fraser River system, which were in the range of 0.53-0.56. Mass 202 PAHs (Flu and Pyr) are common from biomass-focused fire events (Masclet et al., 1995; Jenkins et al., 1996; Oanh et al., 1999; Fine et al., 2001; Schauer et al., 2001). Similarly, both Flu and Pyr are commonly observed from sediments in remote locations and from extracted sediments dated to pre-industrial times (Yunker et al., 1999; 2000).

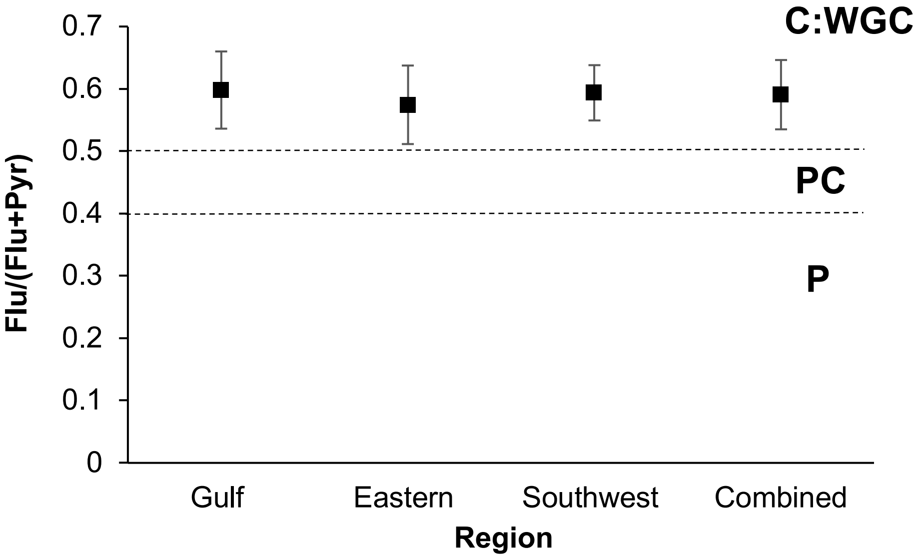


Figure 5.2 PAH diagnostic ratio plot of Flu/(Flu+ Pyr). Standard deviation of the mean is presented. *n*=116, 83, 162, and 361 for the Gulf, Eastern, Southwest and Combined regions, respectively. C: Combustion; WGC: Wood, grass, coal; PC: Petroleum Combustion; P: Petroleum.

The Ant/(Ant+Phe) ratio distinguishes between petrogenic and combustion sources, as values <0.1 indicate petrogenic and those > 0.1 indicate combustion (Yunker et al., 2002). Values among regions ranged from 0.34 to 0.39 for this ratio, all in agreement with combustion sources (Fig 5.3). Yunker et al. (2002) suggest that ratio values for Ant/(Ant+Phe) are expected to be higher in urban areas, with remote areas likely to demonstrate values below or close to 0.1. The values presented for NS SCHs exceed those determined by Yunker et al. (2002) for Vancouver Harbour, which reflected diagnostic ratio values of 0.26 (+/- 0.01), and the Fraser River, which demonstrated values of 0.17 (+/- 0.01). Interestingly, the Flu/(Flu+Pyr) and Ant/(Ant+Phe) ratios appear to be related, as values above 0.4 for Flu/(Flu+Pyr) are often accompanied by values greater than 0.1 for Ant/(Ant+Phe). This relationship is supported by values presented in this study.

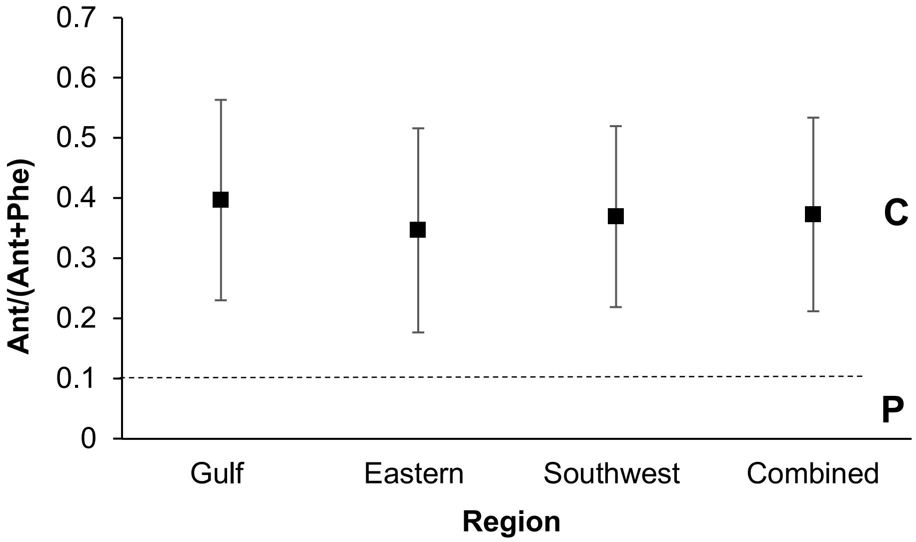


Figure 5.3 PAH diagnostic ratio plot of Ant/(Ant+Phe). Standard deviation of the mean is presented. *n*=116, 83, 162, and 361 for the Gulf, Eastern, Southwest and Combined regions, respectively. C: Combustion; P: Petroleum.

The BaA/(BaA+Chr) ratio provides insight to petrogenic and combustion sources and includes a range for mixed sourcing. Values <0.2 suggest petrogenic sourcing, values between 0.2 and 0.35 indicate mixed sourcing, while values >0.35 are indicative of combustion sources (Yunker et al., 2002). Similarly, Dickhut et al. (2000) indicate that ratio values of 0.53±0.06, 1.11±0.06, and 0.79±0.13 align with automobile emissions, coal/coke, and wood burning processes, respectively. NS SCH regions demonstrate values ranging from 0.41-0.46, all of which indicate combustion sources (Yunker et al., 2002) (Fig 5.4). Standard deviation of the mean among regions indicates that certain individual samples among harbours may reflect ratio values which indicate mixed sourcing. Values >0.35 for BaA/(BaA+Chr) are often accompanied by values >0.4 for the Flu/(Flu+Pyr) ratio for urban locations, which is reflected in this current study (Yunker et al., 2002). In comparison to Dickhut et al. (2000) ratio values, mean ratio values from this study align closely with automobile emissions.

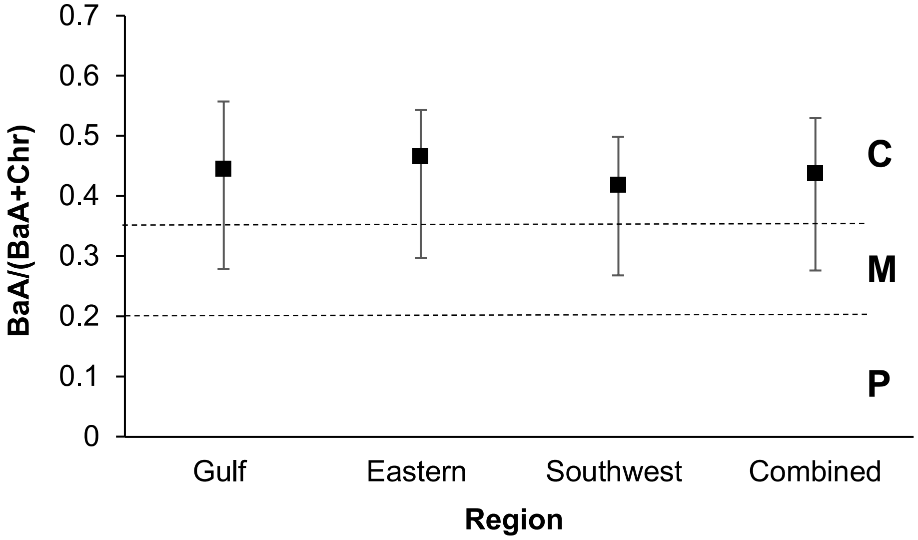


Figure 5.4 PAH diagnostic ratio plot of BaA/(BaA + Chr). Standard deviation of the mean is presented. *n*=127, 86, 189, and 402 for the Gulf, Eastern, Southwest and Combined regions, respectively. C: Combustion; M: Mixed Sources; P: Petroleum.

The IP/(IP+BghiP) ratio provides insight to petroleum, petroleum combustion, and combustion sources. Values <0.2 indicate petroleum, values between 0.2 and 0.5 indicate petroleum combustion, and values >0.5 indicate wood, grass, and/or coal combustion (Yunker et al., 2002). Dickhut et al. (2000) propose values of 0.33±0.06, 1.09±0.03, and 0.28±0.05 for automobile emissions, coal/coke, and wood burning processes, respectively. This ratio demonstrates the greatest variability among regions and values range from 0.22-0.51 (Fig 5.5). The Gulf region demonstrates a value of 0.22±0.34, the Eastern region demonstrates a value of 0.49±0.07, the Southwest demonstrates a value of 0.51±0.05, and the combined regions have a value of 0.43±0.21. Therefore, all regions, excluding the Southwest, demonstrate values in the petroleum combustion range, as per Yunker et al. (2002). The Southwest region presents a value that indicates wood, grass and/or coal combustion (Yunker et al., 2002). In comparison to the values presented by Dickhut et al. (2000), the Gulf region aligns closely with wood burning processes, while the remaining regions align more closely with automobile emissions. A value >0.4 for IP/(IP+BghiP) is often accompanied by values >0.4 for the Flu/(Flu+Pyr) ratio for urban locations (Yunker et al., 2002), a relationship which is partially supported by values in this study.

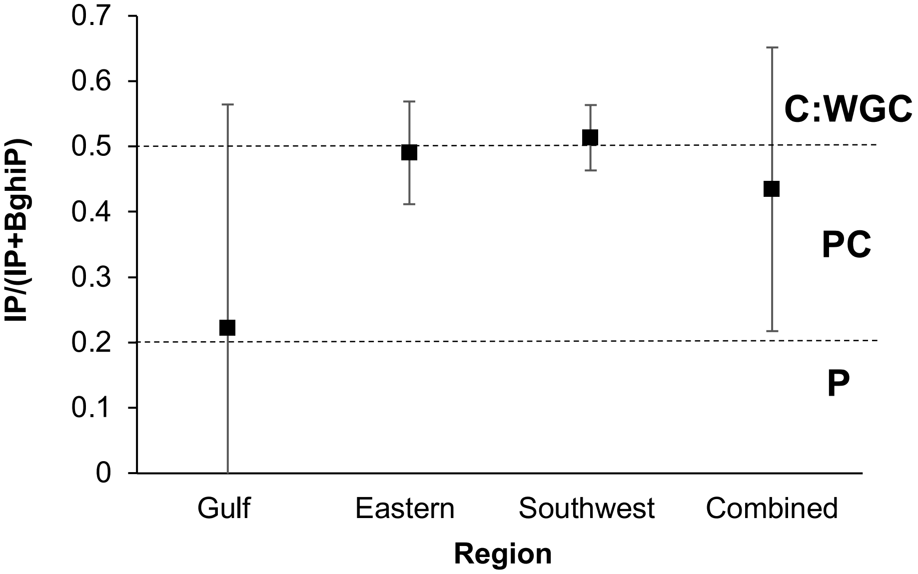


Figure 5.5 PAH diagnostic ratio plot of IP/(IP+BghiP). Standard deviation of the mean is presented. *n*=78, 79, 154, and 311 for the Gulf, Eastern, Southwest and Combined regions, respectively. C: Combustion; WGC: Wood, grass, coal; PC: Petroleum Combustion; P: Petroleum.

Similar diagnostic ratios to those reported in this study have been reported for sediments across other harbour sites in NS over the last 20 years. Surficial sediments of Halifax Harbour (1999) were assessed by single PAH diagnostic ratios, which suggested that combustion sources were the greatest contributors (Hellou et al., 2002). The location of Halifax Harbour is within close proximity (within 200 km) to five of the 31 SCHs in this study. Sediments of the Bay of Fundy were recently assessed by both Flu/(Flu+Pyr) and IP/(IP+BghiP) ratios, both of which indicated that samples were from mixed combustion processes from biomass and fossil/solid fuels (Yang et al., 2018). Multiple stations within Sydney Harbour, NS, sediments have been assessed for PAH emission sources by diagnostic ratios and suggest a strong coal combustion signature based on ratio values (Walker et al., 2015a). Similarly, multiple PAH diagnostic ratios, including BaA/(BaA+Chr) as applied above, have indicated a strong coal combustion and coal handling signature in sediments and soils gathered in and around the Sydney Tar Pond (STP) area in Sydney, Nova Scotia (MacAskill et al., 2016). Ratio analyses by Walker et al. (2017) further support the strong influence of coal combustion as a dominating emission source in Sydney. This site may be particular importance given that seven of the 31 selected SCHs are within 200 km of Sydney, Nova Scotia. Sydney was historically home to a large steel facility and coking operation that produced and emitted vast amounts of contaminants into the surrounding environment, including PAHs (Smith et al., 2009; Walker et al., 2013b; 2013c; MacAskill et al., 2016).

The ratio of LMW to HMW PAHs can indicate between petrogenic and pyrogenic sources. If the ratio of ∑LMW/∑HMW is < 1, this indicates pyrogenic sources, while a value >1 suggests petrogenic sources (Hwang and Foster, 2006; Zhang et al., 2008). NS SCH regions demonstrated values which ranged from 0.32-0.43 (Fig 5.6). All regions demonstrate values which suggest pyrogenic sources.

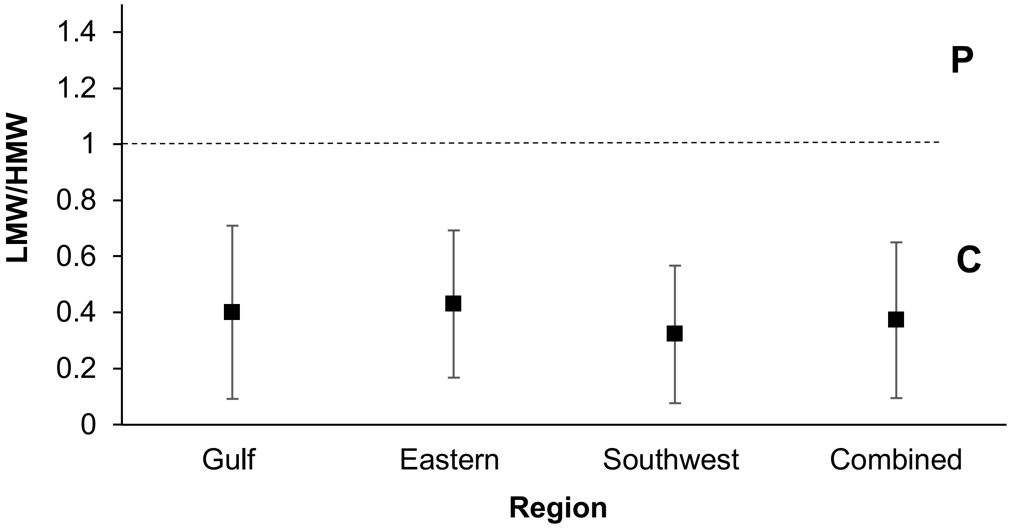


Figure 5.6 PAH diagnostic ratio plot of LMW to HMW PAHs. Standard deviation of the mean is presented. Samples used were *n*= 224, 108, 248, and 580 for the Gulf, Eastern, Southwest and Combined regions, respectively. C: combustion (pyrogenic), P: petrogenic.

The ratio of ∑4 ring PAHs/∑5-6 ring PAHs can provide insight to whether localized or long-range transport processes are dominating the PAH profile at a receptor (Liu et al., 2007; Souza et al., 2018). Values <0.9 indicate localized contributions, while values >0.9 suggest long range transport (Liu et al., 2007). This ratio is applied with the understanding that environmental behaviour of 4 ring PAHs as compared to 5 and 6 ring PAHs is different (Halsall et al., 1997; 2001; Hou et al., 2006). In consideration of transport processes, 5 and 6 ring PAHs only exist in particulate form when emitted to air and are subsequently more likely to undergo degradation in the atmosphere before reaching a receptor (Halsall et al., 1997, 2001; Hung et al., 2005). In contrast, 4 ring PAHs exist in both gas and particulate forms, and therefore may be transported longer distances without the same degree of degradation in the atmosphere (Simoneit et al., 1991; Halsall et al., 2001; Hung et al., 2005). Previous studies have supported this notion and indicate that gaseous phase PAHs are more abundant with LMW PAHs, while particulate PAHs have higher loadings of HMW PAHs (Prevedouros et al., 2004; Liu et al., 2007). In application of this ratio, higher values indicate a predominance of 4 ring PAHs, an indication that long range transport processes may be impacting receptors, while a lower value indicates a dominance of 5 and 6 ring PAHs, suggesting localized sources may be the dominating emission sources. NS SCH regions demonstrated values which ranged from 2.18-3.17 (Fig. 5.7), consistently demonstrating values that suggest long-range transport emissions.

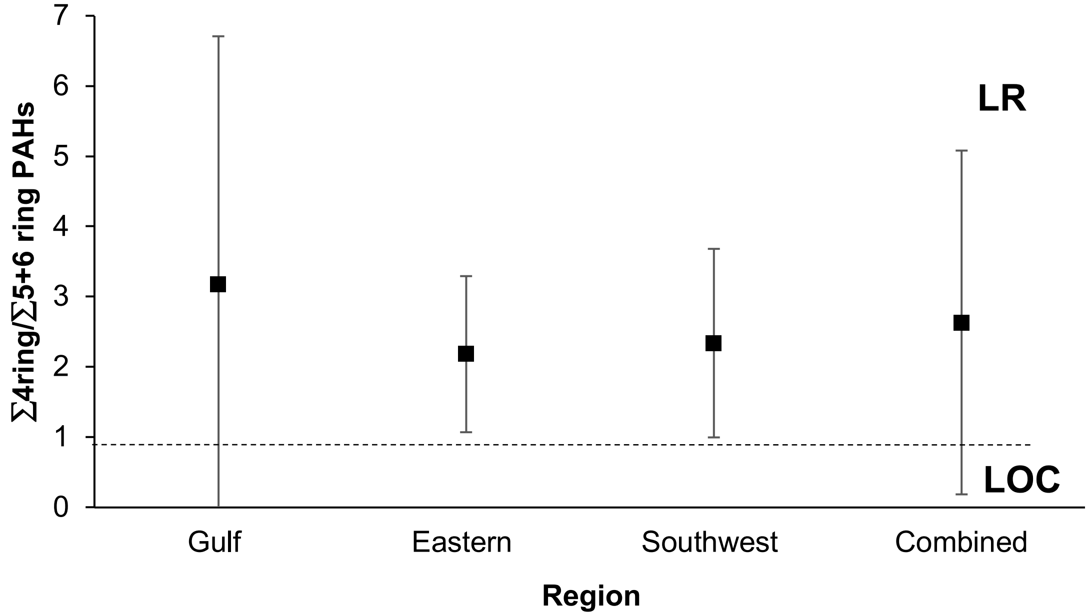


Figure 5.7 PAH diagnostic ratio plot of ∑4 ring PAHs to ∑5+6 ring PAHs. Standard deviation of the mean is presented. Samples used were *n*= 224, 108, 248, and 580 for the Gulf, Eastern, Southwest and Combined regions, respectively. Abbreviations include: LOC: localized, LR: long-range.

The diagnostic ratios applied above suggest that PAH combustion sources most greatly impact NS SCH sediments. This is further supported by assessment of diagnostic ratios applied to sediments in other harbours in NS that also demonstrate a strong combustion signature, strongly linked to coal-related processes. The ratio of ∑4 ring PAHs/∑5-6 ring PAHs indicates values that suggest PAHs are more likely to be the product of long-range transport processes, as compared to localized inputs. The results of this ratio are supported by results detailed by Xu (2018) in the Alberta oil sands, in that PAH concentrations deceased with increasing distance from known sites which were contributing pet-coke dust.

5.3.2 Source Apportionment Using Unmix O

Unmix O identified four factors (sources) which best describe PAHs in NS sediments **(**Table 5.2). Factor 1 and Factor 2 contribute 32 and 47%, respectively, to the total PAHs among samples, while Factors 3 and 4 contribute to a much lesser extent at 11 and 10%, respectively. Similarly, Fig. 5.8 further supports that Factor 1 and 2 are the most dominant factors characterizing NS SCH sediments, as reflected by the high number of individual samples clustering near the vertices and between vertices of these two factors.

Table 5.2 Percentage of total PAH (TPAH) and individual PAH species in each Unmix factor (source) (Comp. is an abbreviation for composition).

	Factor 1		**Factor 2**		**Factor 3**		**Factor 4**	
Compound	**Comp.**	**%**	**Comp.**	**%**	**Comp.**	**%**	**Comp.**	**%**
TPAH	1.67	32	2.43	47	0.588	11	0.521	10
Ace	0.00205	0.1	0.00332	0.1	0.000661	0.1	0.0696	13.4
Ant	0.0025	0.1	0.0133	0.5	0.224	38.1	0.000479	0.1
BaA	0.179	10.7	0.23	9.5	0.00141	0.2	0.00711	1.4

	Factor 1		Factor 2		Factor 3		Factor 4	
Compound	**Comp.**	**%**	**Comp.**	**%**	**Comp.**	**%**	**Comp.**	**%**
BaP	0.247	14.8	0.0642	2.6	0.00151	0.3	0.00581	1.1
BbF	0.246	14.7	0.0531	2.2	0.00895	1.5	0.0102	2.0
BghiP	0.128	7.7	0.00171	0.1	0.00636	1.1	0.00508	1.0
BkF	0.231	13.8	0.00327	0.1	0.0237	4.0	0.00373	0.7
Chr	0.342	20.5	0.139	5.7	0.0197	3.4	0.0173	3.3
Flu	0.00434	0.3	1.13	46.5	0.00806	1.4	0.00124	0.2
Fl	0.00312	0.2	0.0018	0.1	0.0353	6.0	0.061	11.7
IP	0.119	7.1	0.028	1.2	0.00361	0.6	0.000188	0.0
Phe	0.0109	0.7	0.0129	0.5	0.212	36.1	0.163	31.3
Pyr	0.0356	2.1	0.693	28.5	0.0339	5.8	0.0282	5.4

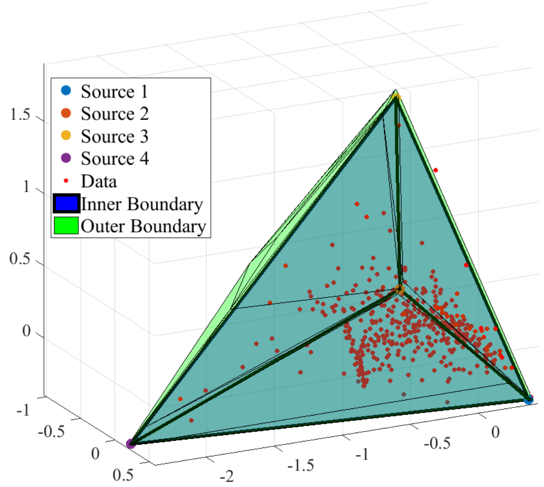


Figure 5.8 A 3-dimensional view of the four factors identified by Unmix O and the location of individual samples (red dots) with respect to each factor. Each factor is presented by vertices as part of the tetrahedron. The inner and outer boundaries (as defined by the model) of this area are presented.

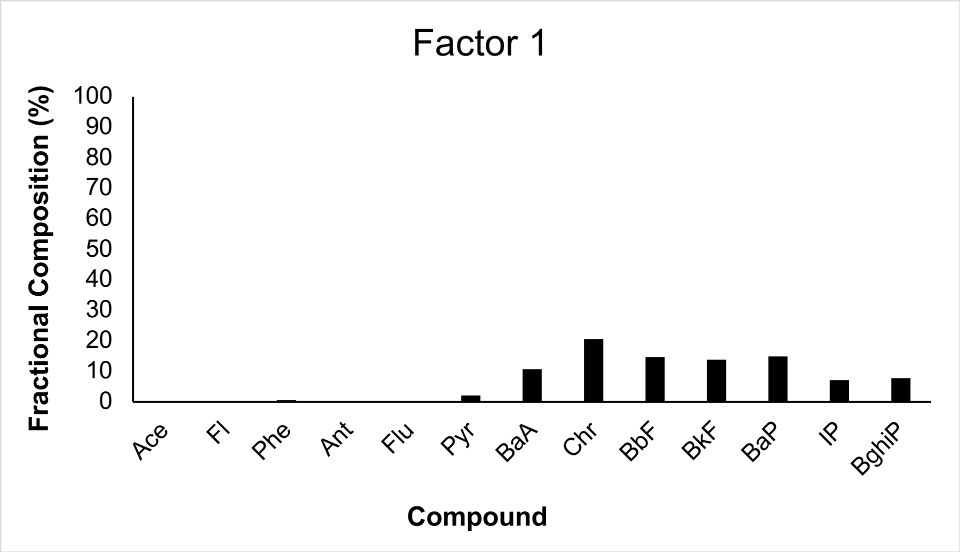
Factor 1 is characterized by high loadings of HMW PAHs, including Chr, BbF, BkF, BaP, IP and BghiP (Fig 5.9a). Normalized square difference (Chi^2 sum calculations) indicate a closeness to profiles from the greater literature (see Van Metre and Mahler, 2014), and a lower calculated value indicates similarity between profiles. Coke oven emissions (Chi^2 sum=155.76), coal tar sealant profiles (174.07, 281.23, 329.83), traffic tunnel air (374.80), and gasoline vehicle particulate emissions (418.71) profiles demonstrated the lowest Chi^2 sum calculation when compared to Factor 1. Diagnostic ratio plots of factor 1 as compared to the 22 source profiles (Van Metre and Mahler, 2014) indicate similar locations to traffic tunnel air, coal average, and residential heating profiles. The large proportion of IP, BghiP, and BbF and BkF suggest vehicular emissions (Duval and Friedlander, 1981). Similarly, Chr, BaP, BaA are compounds which suggest coal combustion (Duval and Friedlander, 1981, Larsen and Baker, 2003, Sofowote et al., 2008). *Factor 1 is estimated to be a mixed source representative of coal combustion and vehicular emissions.*

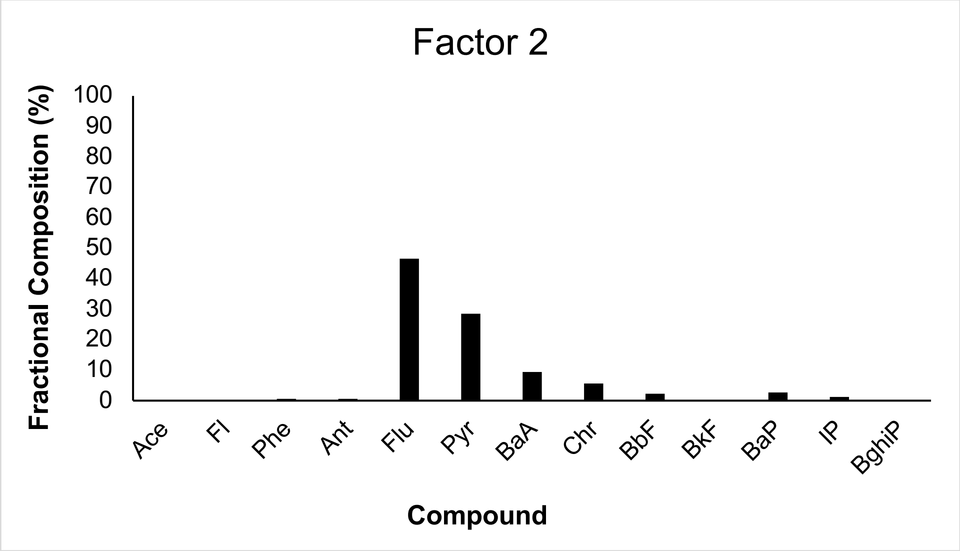
Factor 2 is characterized by high loadings of Flu and Pyr and to a lesser extent, BaA and Chr (Fig 5.9b). Similar to Factor 1, Factor 2 is dominated by HMW PAHs. Normalized square difference (Chi^2 sum calculations) indicate a closeness to pine-wood soot particles from the greater literature (389.25). Ratio plots indicate factor 2 is similar to used motor oil, fuel oil combustion particles, and pine wood soot particles. The four ring PAHs which dominate factor 2 are often produced by the burning of biomass, coal combustion, or industrial/residential incineration processes (Simoneit et al., 2005, Ravindra et al., 2006a). The dominating PAHs of this factor [Flu, Pyr, BaA and Chr] are considered tracers for coal combustion processes as well (Duval and Friedlander, 1981). *Factor 2 is estimated to be a biomass/coal combustion source.*

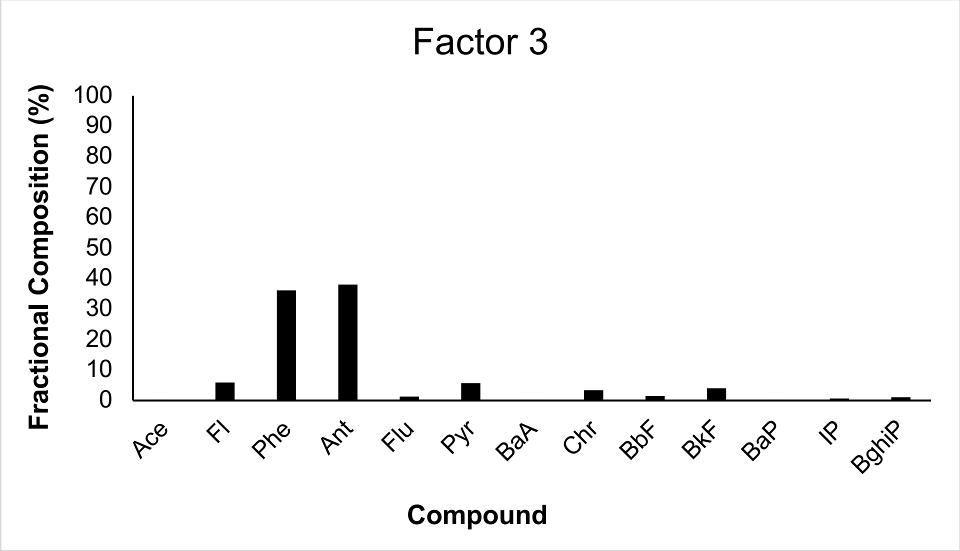
Factor 3 has high loadings of Phe and Ant and is dominated by higher loadings of LMW PAHs (Fig 5.9c). Normalized square difference (Chi^2 sum calculations) indicate a closeness to many of the 22 literature profiles (Van Metre and Mahler, 2014), as the calculated values remain close to another. Residential heating (141.72), used motor oil profiles (147.83 and 164.22), and coal tar (169.44) are the most closely related profiles. Ratio plots indicate factor 3 is similar to gasoline vehicle particulate emissions, tire particles, and traffic tunnel air. Phe and Ant, which present the highest loadings in this factor, can be indicators of biomass burning, coal combustion, and coke production

(Duval and Friedlander, 1981; Harrison et al., 1996). *Factor 3 is estimated to be a mixed petrogenic-dominated source (i.e. motor/hydraulic oil)*

Factor four is characterized by high loadings of Phe, Ace, and Fl and is dominated by higher loadings of LMW PAHs (Fig 5.9d). Normalized square difference (Chi^2 sum calculations) indicate a particular closeness to 15 of the 22 literature profiles, as the calculated values remain close to one another. Diesel particles (109.78), residential heating (147.75), diesel vehicle particulate emissions (153.71), and coal tar (203.54) indicate the greatest similarity to factor 4. Ratio plots indicate factor 4 is similar to tire particles, gasoline vehicle particulate emissions, and asphalt profiles. Diesel boat engines have also demonstrated the Phe and Fl are commonly emitted in elevated concentrations (as compared to other PAHs) in both particulate and gaseous form from engine exhaust (Lin et al., 2006; Hsieh et al., 2009). Fl and Phe, two of the highest loadings, are dominant within coal (Achten and Hoffman, 2009). Similarly, Phe can be emitted from biomass burning, coal combustion, and coke production sources (Duval and Friedlander, 1981, Harrison et al., 1996; Wang et al., 2013). *Factor 4 is estimated to be a mixed source of petrogenic and pyrogenic origins.*




Factor 2
Fractional Composition (%)
100
90
80
70
60
50
40
30
20
10
0
Ace
Fl
Phe
Ant
Flu
Pyr
BaA
Chr
BbF
BkF
BaP
IP
BghiP
Compound


Factor 3
Fractional Composition (%)
100
90
80
70
60
50
40
30
20
10
0
Ace
Fl
Phe
Ant
Flu
Pyr
BaA
Chr
BbF
BkF
BaP
IP
BghiP
Compound

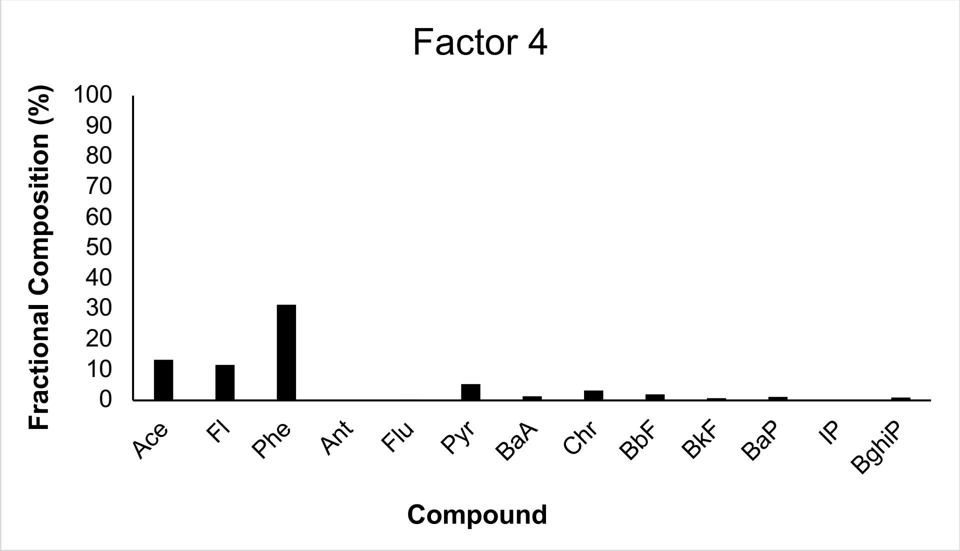

Factor 4
Fractional Composition (%)
100
90
80
70
60
50
40
30
20
10
0
Ace
Fl
Phe
Ant
Flu
Pyr
BaA
Chr
BbF
BkF
BaP
IP
BghiP
Compound

Figure 5.9 (a-d) Fractional composition of 14 individual PAH species in a) Unmix O Factor 1; b) Unmix O Factor 2; c) Unmix O Factor 3; d) Unmix O Factor 4.

5.3.3 Source Apportionment by PAH Profile Composition Assessment

Fig. 5.10 shows the distribution of 2-6 ring PAHs among samples in the Gulf, Eastern, and Southwest regions of NS. The distribution of PAHs in each category (%) is very similar across regions. Four ring PAHs dominate, with three ring and five ring PAHs forming the second and third largest categories. HMW PAHs (4-6 ring) generally dominate the sediment samples, while LMW PAHs (2-3 ring) comprise a smaller proportion. This distribution aligns with the ratio presented in Fig. 5.6, that further reflects the larger proportion of HMW PAHs, as compared to LMW PAHs. The abundance of HMW PAHs is an indication that combustion processes are likely the dominating source in the PAH profile of NS SCH sediments as high temperature combustion sources often produce HMW PAHs (Mosert et al., 2010). Similarly, there is increased likelihood of HMW PAHs (often produced by high temperature combustion) entering aquatic environments directly through deposition, as compared to LMW PAHs (McCready et al., 2002). Furthermore, in aquatic environments, HMW PAHs are more likely to maintain their integrity, because of the carbonaceous matter they associate with (soot, black carbon, char) can provide protection from degradation (Yunker et al., 2002; Achten and Hoffman, 2009; Tobiszewski and Namieśnik, 2012; Yunker et al., 2011, 2014). This relationship supports the increased accumulation of HMW PAHs in sediments and their persistence in aquatic environments (Koelmans et al., 2006; Achten and Hoffman, 2009; Yunker et al., 2014).

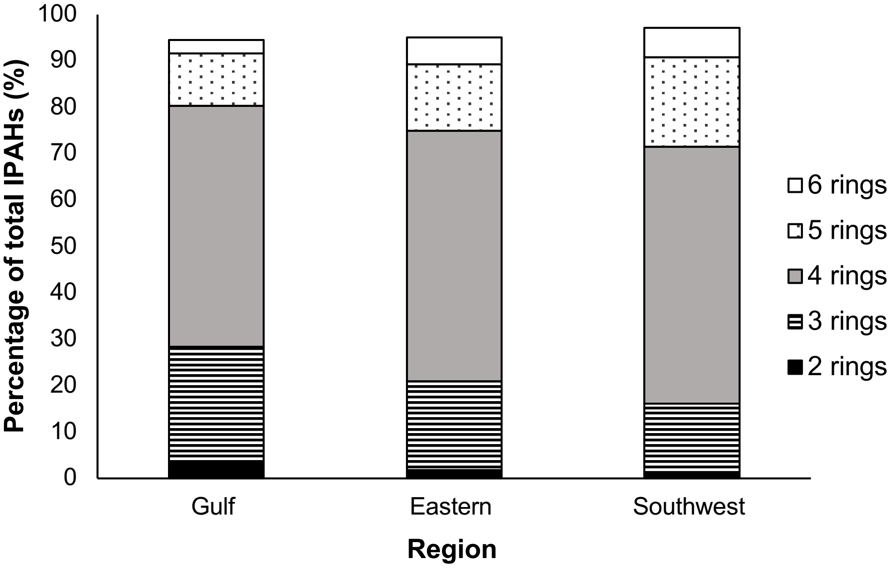


Figure 5.10 Compositional assessment of PAHs in sediments of NS SCHs by the number of atomic rings. US EPA Priority 16 PAHs were included within the atomic ring categories, while 1 and 2-methylnapthalene (1-MN and 2-MN) and perylene (pery) were excluded. Concentrations of these compounds (1-MN, 2-MN and pery) were included to calculate the total PAH value however, and subsequently form the remaining percentage for each region.

The dominance of HMW PAHs in surficial sediments within Atlantic Canada, especially the dominance of fluoranthene and pyrene, has been widely observed. Previous studies of sediments along the Bay of Fundy (of which 5 of the current study 31 SCHs reside) have supported these findings (Hellou et al., 2005; Yang et al., 2018). Similarly, surficial sediments of Halifax Harbour demonstrate the same trend (Hellou et al., 2002). Previous work by Davis et al. (2018) indicates that this holds true for the 31 NS SCHs of this current study, as fluoranthene and pyrene are the top two dominating PAHs among all sediment samples, followed by phenanthrene.

The relationship between typical combustion PAHs [$\sum$Comb] and the $\sum PAH_{16}$ value among samples is represented in Fig. 5.11. PAHs which are typically produced from combustion processes include: Flu, Pyr, BaA, BbF, BkF, BaP, DBahA, BghiP, and IP (Prahl and Carpenter, 1983). All of these compounds are HMW and contain between 4 and 6 rings. Pearson correlation analysis indicated a strong positive relationship between $\sum$Comb and $\sum PAH_{16}$ (r^2= 0.958, n=580). This relationship is best interpreted as the dominance of combustion derived PAHs as part of the total PAH profile among sediment samples. Davis et al. (2018) have identified that many of the combustion associated PAHs above are present in NS SCH sediments in the greatest concentrations, particularly Flu and Pyr. As such, one would expect to see a positively correlated relationship between combustion PAHs (which are HMW) and total PAHs of a sample as these compounds are expected to form the greatest proportion.

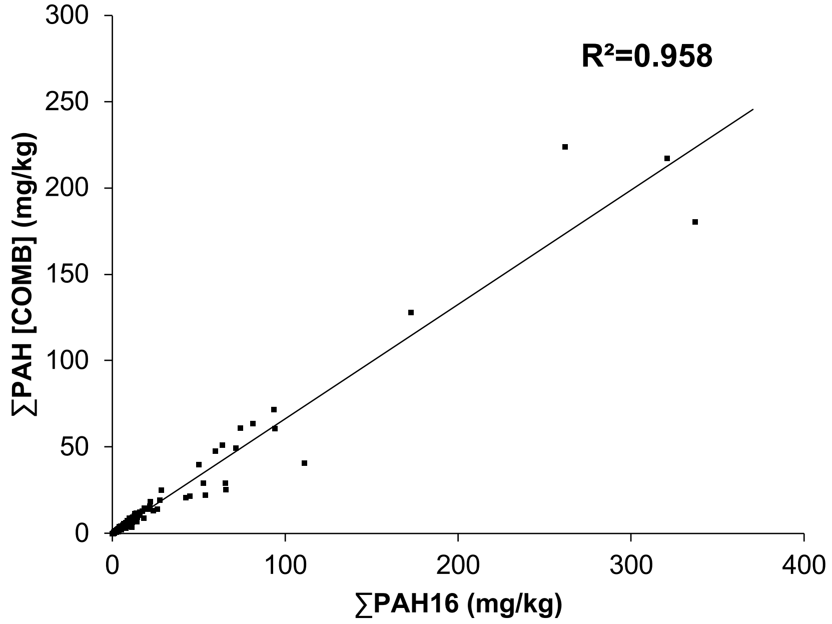


Figure 5.11 Correlation analysis between ∑COMB PAHs and $\sum PAH_{16}$ in SCH sediments in NS. ∑COMB PAHs is the sum of [Flu, Pyr, BaA, BbF, BkF, BaP, DBahA, BghiP], while $\sum PAH_{16}$ encompasses the 16 PAHs listed as US EPA priority pollutants. Coefficient of determination (R^2) is presented (*n*=580).

PAH profile compositional assessment of PAHs in other sediments in Atlantic Canadian harbours have further suggested the dominance of combustion sources. Molecular abundance and carbon isotope assessment of PAHs in sediments within St. John's Harbour in Newfoundland, Canada, had previously indicated that the majority of PAHs present were of combustion origins, with vehicular emissions suggested as the dominating source (O'Malley et al., 1996). Similarly, sediments assessed in the Bay of Fundy showed a greater abundance of 3-6 ring PAHs, as compared to 2-3 ring PAHs, indicating a greater abundance of HMW PAHs, suggesting that they were produced by combustion sources (Yang et al., 2018).

5.3.4 Source Estimation Using Multiple Lines of Evidence

The multiple lines of evidence employed to investigate source apportionment strongly indicate that NS sediments are dominated by combustion (pyrogenic) PAH compounds, with petrogenic PAHs contributing at a much smaller extent. PAH diagnostic ratios overwhelmingly suggest sediment samples contain PAHs that are produced by means of combustion sources, including in certain cases, wood, grass [biomass] and/or coal combustion processes. However, the ratio of IP/(IP+BghiP) indicated petroleum combustion may contribute to NS sediments. This line of evidence supports the notion that combustion processes are a dominating source, yet petrogenic inputs are still an important consideration among samples. One PAH diagnostic ratio (∑4 ring PAHs/∑5-6 ring PAHs) indicates that PAHs in NS SCH sediments are most likely a product of long range transportation processes, as compared to localized inputs. Historically, the majority of historical coal combustion processes were centralized to the Cape Breton region of NS due to the large steel facility that operated for nearly a decade (Ferrara et al., 2007; MacAskill et al., 2016). Currently, NS has four coal and/or pet coke powered plants responsible for part of the province's power generation (Fig. 5.1). The plants are located in Lingan, Point Aconi, Point Tupper, and Trenton (NS Power, 2017). Of these plants, three (Lingan, Point Aconi and Point Tupper) are located on Cape Breton Island and would be in closest proximity to eastern region *(n*=6*)* SCHs. Trenton, NS, is most closely situated to SCH sites in the Gulf region *(n*=9*).* Specific to PAH concentrations and proximity to potential emission sources, a study conducted in the Alberta oil sands demonstrated that PAH concentrations deceased with increasing distance from known sites which were contributing pet-coke dust (Xu, 2018). Therefore, it could be expected that PAHs that are the product of coal or pet coke combustion processes may reside in harbours with close proximity to these sites. With this information in mind, it can be inferred that some PAHs across NS are likely mobile, yet the distance in which they may be transported is very reliant on a variety of other factors (wind, emission sources).

Future studies could incorporate these variables into source apportionment investigations to elucidate greater resolution of potential sources of PAHs.

The four PAH sources identified by Unmix O indicate large contributions of pyrogenic origin, with a smaller contribution of petrogenic origin. Factors 1 and 2 are dominated by HMW PAHs and contribute the greatest amount to total PAHs among sediment samples. Factor 1 is likely a coal combustion/vehicle emission source, while Factor 2 suggests a coal combustion/biomass incineration signature. Factors 3 and 4 are both estimated to be dominated by petrogenic input and contribute to the total PAH profile to a much smaller extent. These sources indicate the importance of coal combustion as part of the NS PAH signature in sediments. Both Factor 1 and 2 (which contribute the most to the total PAH profile) demonstrate individual PAH loadings which suggest this process is a key contributing factor to sediment PAH levels. Similarly, Factor 4 demonstrates PAH compounds which are tracer compounds for coke production, which may be a historical indication related to the former coke ovens associated with a steel facility that operated for decades in Cape Breton (Ferrara et al., 2007; MacAskill et al., 2016).The strong signature of coal combustion aligns with source apportionment studies previously completed in NS (MacAskill et al., 2016).

Biomass incineration and vehicular emissions also demonstrate strength as PAH emission sources contributing to NS SCH sediments. Biomass incineration may contribute given that burning (incineration) of biomass is a very common practice in the province of Nova Scotia. Residential burning of wood through wood stoves or furnaces is a favorable option for Nova Scotians because it is cost-effective and can reduce the heating bill for residents (Efficiency Nova Scotia, 2018). Similarly, a study completed by Natural Resources Canada Office of Energy Efficiency in 2009 indicated that residents of NS drive the furthest distances in their vehicles as compared to all other provinces (NRCAN, 2009). The geography of the province is likely a contributor, as alternative transportation options are limited in many regions of the province. The average household has at least one vehicle, and the city of Halifax is home to more than 40% of the province's population (NRCAN, 2009). Therefore, the increased usage of vehicles by NS residents may be a contributing factor of vehicular emission PAHs in SCH sediments.

It can also be noted that regular boat traffic by fishing vessels at SCH sites may be a small contributor of ‘vehicular emission’ PAHs, of which are emitted from a diesel engine, yet boat exhaust is not estimated to be dominating source. Unmix O source 4 demonstrates high loadings of compounds (Fl, Phe) which are known to be contributed into harbour environments by diesel boat engines, yet it is well understood that naphthalene (Nap) is the PAH compound which may be considered the strongest indicator of this emission source as it is generally emitted in concentrations which are far greater than Fl or Phe from a diesel boat engine. Unfortunately, Nap was excluded from the Unmix model which makes diesel boat engine emissions difficult to estimate. However, assessed Nap concentrations among SCHs were relatively low in comparison to Fl and Phe, and of all assessed PAHs, Nap demonstrated the lowest number of exceedances when compared to sediment quality guidelines, which may be directly related to the known volatility of the PAH compound (Davis et al., 2018). As Unmix O Factor 4 contributes only 10% to the total PAHs among samples, this further suggests that the potential impact of diesel engine emissions from SCH vessels may be a minimal source contributor to PAHs in sediment.

The four factors identified by Unmix O are characteristic of all samples, across all regions of NS, which supports the notion that combustion processes are likely impacting SCHs that are not in close proximity. Assessment of the composition of the PAH profile of samples further supports the findings of the diagnostic ratios and Unmix O. HMW PAHs dominate samples, with LMW PAHs contributing to a lesser extent. HMW PAHs tend to dominate the urban background PAH profile, which is often comprised of 4-6 ring PAHs, and occurs from storm water run-off and other non-point sources including incineration and vehicular emissions (Van Metre et al., 2000; Yunker et al., 2002; Stout et al., 2004). This further supports the dominating role of combustion PAHs (pyrogenic) in NS sediments.

5.4 CONCLUSION

This study investigated source apportionment of PAHs in NS sediments across 31 SCHs, by employing three lines of evidence. The three lines of evidence support the notion that NS sediments are most impacted by combustion sources, likely attributed to historical coal combustion processes and the strong history of coal production in the province, and further supported by current and historical residential incineration of wood products and vehicular usage by Nova Scotian residents. Petrogenic sources appear to affect NS sediments as well, yet to a much lesser extent, as reflected in both the diagnostic ratios and the two smaller sources identified by Unmix O. Results further support that the PAH inputs to NS sediments are likely characterized by historical coal combustion processes and urban background inputs, especially vehicular emissions and biomass combustion in the residential setting. It is likely PAHs are a product of both long range and localized inputs, given the dominance of coal combustion, alongside vehicular emissions and residential burning sources which can contribute both locally or at a distance. The PAH profile of NS sediments is dominated by high molecular weight PAHs, likely produced by high temperature combustion processes, which is similar to many regions of the world.

Acknowledgements:

This study was made possible by data kindly supplied by DFO-SCH and PSPC. Funding was provided by the Province of Nova Scotia (NS Graduate Scholarship) and the School for Resource and Environmental Studies, Dalhousie University. This work was supported by NSERC Discovery Grant RGPIN-2018-04119 to T.R.W. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

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CHAPTER 6 CONCLUSIONS: MANAGEMENT IMPLICATIONS FOR PAHs IN NS SCH SEDIMENT

6.1 SUMMARY OF RESEARCH

This research aimed to characterize and assess polycyclic aromatic hydrocarbons (PAHs) in Nova Scotia (NS) small craft harbour (SCH) sediments. Three research objectives were defined in support of this research.

- The first objective was to characterize the distribution of PAHs in NS SCHs at the individual harbour level and across the Gulf, Eastern, and Southwest regions of NS. This was achieved through comparison to sediment quality guidelines (SQGs), statistical analysis, and by analysis of aggregate/individual PAH concentrations (described in Chapter 4)
- The second objective was to assess source apportionment of PAHs across NS SCHs by employing multiple lines of evidence. This objective was achieved by applying PAH diagnostic ratios, US EPA Unmix Optimum receptor modelling, and PAH profile composition assessment (described in Chapter 5)
- The third objective was to form evidence-based recommendations to support SCH management in NS and beyond, particularly in terms of prioritizing SCHs and efficient use of federal government spending.

To accomplish this, recommendations were formulated based on results presented in support of objectives one and two. In addition, this work has further solidified the importance of the Marine Sediment Sampling Program (MSSP) as a management tool in assessment of PAHs (and other contaminants) in SCHs. As such, limitations of the MSSP that directly influence PAH assessment/characterization in SCHs are discussed, and recommendations for improvement of the MSSP are provided in section 6.4.

This chapter provides a summary of the key findings of this research, provides management-specific recommendations, discusses the limitations and challenges of this study, and reflects on future research that could be derived from this study.

6.2 SIGNIFICANT FINDINGS

This study has resulted in three key findings:

1. Sediment in SCHs reflect low $\sum PAH_{16}$ concentrations, with only 2 SCHs indicating $\sum PAH_{16}$ concentrations >NOAA ERM guideline
2. High molecular weight PAH compounds dominate NS SCH sediments
3. PAHs in NS SCH sediments are primarily of pyrogenic origin, including processes such as coal combustion, biomass combustion, and vehicular emissions

These findings are expanded upon below and discussed with management implications in mind. When applicable, recommendations specific to the management of PAHs in SCHs are discussed.

6.3 MANAGEMENT IMPLICATIONS AND RECOMMENDATIONS

6.3.1 Assessment of $\sum PAH_{16}$ Concentrations

The majority of sediments in the assessed SCHs presented low $\sum PAH_{16}$ concentrations, indicating that impairment to biota is unlikely as per the National Oceanic and Atmospheric Administration (NOAA) effect range median (ERM) guidelines for total PAHs. Only two harbours, Canso (Eastern region) and Fox Point (Southwest region) exhibited $\sum PAH_{16}$ concentrations which exceeded the ERM guideline. From a management perspective, this suggests that the majority of sediments in NS SCHs are not greatly contaminated by PAHs and may subsequently pose little risk to biota. However, this finding also suggests that SCH managers in NS should prioritize Canso and Fox Point as part of their SCH management strategy. These SCH sites appear to be "outliers" within the province compared to other SCHs assessed, as they exhibit high PAH concentrations which deviate from the majority of other SCHs. This suggests that there may be historical or current sources (e.g., spills) in which PAHs have entered or are continuously impacting these SCH sediments, leading to elevated concentrations.

Recommendation: *SCH managers in NS should prioritize Canso and Fox Point to further delineate PAH contamination.*

6.3.2 Use of $\sum PAH_{16}$ as a Tool for PAH Assessment

In this study, a calculated $\sum PAH_{16}$ for each harbour was used to compare PAH concentrations between individual SCHs and to make inference between regions of NS. Similarly, it was used in comparison to NOAA sediment quality guidelines (SQGs) to provide insight to whether the total PAH concentration was likely to impair biota. The MSSP only calculates total PAHs to compare to Canadian Environmental Protection Act (CEPA 1999) Disposal at Sea Regulation Guidelines and the program primarily focuses on single PAH compound comparisons to SQGs to determine potential exceedances (CEPA, 1999). In review of sediment sampling reports (n=115) used as part of this study, the total PAH value which is calculated for CEPA often reflects the 16 US EPA priority PAHs and excludes 1- and 2- methylnaphthalene and perylene from the 19 total PAHs which are assessed. Therefore, the calculation and comparison of $\sum PAH_{16}$ to NOAA SQGs may prove to be a coarse screening tool for SCH managers, that could easily be integrated into the current MSSP format.

As the Canadian Council of Ministers of the Environment (CCME) do not currently outline a guideline for total PAHs, the adoption of a total PAH guideline value from another jurisdiction presents an opportunity to easily compare NS SCH sediments by assessment of the aggregate PAH profile concentration. NOAA describes effect range low (ERL) and effects range median (ERM) values for total PAHs, and similarly, the province of British Columbia (BC) outlines lower and upper guideline values for total PAHs. This approach aligns with the notion that PAHs are emitted as mixtures into the environment, a characteristic that is more accurately captured by a total PAH value and guideline (Tobiszewski and Namieśnik, 2012). The NOAA ERM and BC upper level guidelines are less conservative that the NOAA ERL and BC lower level counterparts and could provide federal SCH custodians with insight to which SCHs may require the most attention, specific to sediment disposal options and predicted ecological risk for biota inhabiting the SCH (MacDonald et al., 1996; Long et al., 1998).

Recommendation: *The adoption of a total PAH sediment quality guideline (e.g., ERM for* $\sum PAH_{16}$*) may demonstrate utility as a coarse screening tool to identify which SCHs are of highest priority.*

6.3.3 Assessment of Individual PAHs

It was determined that six individual PAHs (fluoranthene (Flu), pyrene (Pyr), phenanthrene (Phe), chrysene (Chr), benzo(a)anthracene (BaA) and benzo(b+k) fluoranthene [B(b+k)F]) dominate NS SCH sediments in the Gulf, Eastern and Southwest regions (Chapter 4). These compounds contribute over 70% to the PAH profile (on a concentration basis) and demonstrate the most elevated concentrations among all PAHs in the profile. All of these compounds, with the exception of phenanthrene, are considered to be high molecular weight (HMW) PAHs, indicating they contain four or more atomic rings. Similarly, PAHs which are characterized by 4,5, or 6 rings (HMW) make up a greater proportion among NS SCH regions as compared to PAHs characterized by 2 or 3 rings (low molecular weight LMW)) (Chapter 5). This evidence indicates that the dominance of HMW PAHs is expected for individual NS SCHs. This trend is common and has been identified in other harbours in Canada and around the world (Zitko, 1999; McCready et al., 2000; Bolton et al., 2004; Vagge et al., 2018).

LMW and HMW PAHs can demonstrate differences in bioavailability that may impact their behavior in aquatic environments. Generally speaking, HMW PAHs may show decreased levels of bioavailability in the aquatic environment as compared to LMW PAHs as they often bind tightly to sediments and can remain physiochemically “stabilized” (Thorsen et al., 2004; Koelmans et al., 2006; Chen and Chen, 2011). This behavior can lend itself to the persistence of high molecular weight PAHs in sediments (Koelmans et al., 2006; Achten and Hoffman, 2009; Yunker et al., 2014).

With respect to maintenance dredging activities which regularly occur at NS SCHs, the understanding of PAH behavior in aquatic environments based on molecular weight is an important consideration in the assessment of PAHs in NS SCHs. This is because it is widely acknowledged that HMW PAHs bound to sediment can become re-suspended and increasingly available to biota from events that disturb the sediment, including dredging (Zheng et al., 2012; Shang et al., 2013). Similarly, dredging can result in the release of accumulated PAHs in sediments that may have negative implications for the harbour environment (Merhaby et al., 2015; Vagge et al., 2018). From an ecological risk perspective, the management of PAHs in SCH sediments may be best addressed by leaving them undisturbed. However, this approach, unfortunately, is not feasible for NS SCHs which must undergo dredging activities for navigational purposes.

Therefore, recognizing that NS SCH sediments are abundant in HMW PAHs, likely stabilized in the sediment matrix, minimizing dredging events is one potential management approach in which the potential risk of PAHs to biota in SCHs can be reduced. However, since dredging is necessary for NS SCHs for navigation and maintenance purposes, it is suggested that managing PAHs in sediment should incorporate both sediment characterization (as satisfied by the MSSP) and dispersion monitoring via water quality sampling and subsequent analysis during dredging, as they are both deemed as important activities that contribute to environmental protection (Casado-Martinex et al., 2006). Currently, dispersal monitoring for contaminants, including PAHs, is not completed for SCHs during dredging activities. The potential risk of PAHs to biota from dredging activities could also be reduced by considering the activity and ecology of aquatic species in dredge planning (e.g., movement patterns, feeding activity of aquatic species). For example, in understanding the behavior of species which may reside in SCHs, or use SCHs as part of their geographical range, dredging during a certain month or season may reduce the potential risk re-suspended PAHs can pose to biota.

Recommendation: *To best manage PAHs in SCHs, minimize dredging events as much as possible, explore the feasibility of contaminant dispersion monitoring technologies, and* *develop an increased awareness of marine biota ecology and behavior when planning dredging activities.*

6.3.4 Assessment of Sediment Quality Guidelines (SQGs)

SQGs are a valuable tool in interpreting sediment quality data. However, SQGs are not always defined for all potential contaminants. Currently, the CCME and NOAA outline individual SQGs for 13 individual PAHs. As such, certain PAHs included as the US EPA 16 priority PAHs, do not have guideline values to aid in the interpretation of their presence. The three compounds of the US EPA 16 which do not have SQG values (e.g., ERL, ERM, ISQG, PEL) defined by the CCME or NOAA include benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), and indeno(1,2,3-cd)pyrene (IP). As described in section 6.3.3, both BbF and BkF contribute greatly to the PAH profile of NS SCH sediments. The lack of SQGs for these three compounds is of particular concern as these PAHs are all characterized as potentially carcinogenic and are US EPA priority pollutants (Long et al., 1995; US EPA, 2014; Van Metre and Mahler, 2014). Some individual Canadian provinces outline SQGs for various contaminants in marine environments which may compensate for the lack of marine SQGs outlined by CCME. For example, British Columbia outlines marine SQGs for benzofluoranthenes that could potentially be adopted and used for NS SCHs, following a review of their technical basis.

Recommendation: *To compensate for the lack of sediment quality guidelines for individual PAHs in aquatic environments, seek guidelines (when appropriate) from other jurisdictions for interpretation of SCH sediment assessments.*

6.3.5 Assessment of PAH Sources

It is estimated that PAHs in NS SCH sediments are primarily of pyrogenic (combustion) origin (Chapter 5). Estimated sources of PAHs in NS SCH sediments include biomass, coal, and vehicular emission sources, that are consistent across the province. This aligns with trends identified in the literature as pyrogenic PAHs are the dominating source of PAHs in the global environment (Wang et al., 2001; Lima et al., 2005; Stout et al., 2015).

From a management perspective, pyrogenic PAH sources are more difficult to define (as compared to petrogenic sources) and subsequently control for a few different reasons. First, pyrogenic PAHs are commonly released first into the atmosphere by an emission source and then they subsequently find their way into other environments (Doong and Lin, 2004; Stout and Emsbo-Mattingly, 2008). Similarly, there are many high temperature combustion sources that can produce pyrogenic PAHs, and they can travel distances by wind or urban run-off, making their initial release difficult to define (McCready et al., 2000). Despite this, in the NS context, understanding that pyrogenic PAHs most greatly exist in SCH sediments is a valuable piece of information for federal custodians of SCHs. The results of this study (detailed in Chapter 5) indicate that many of the sources contributing PAHs to SCH sediments are not likely associated with the daily activities conducted at SCH sites. As SCHs are federally managed sites, this reduces the federal environmental liability of PAH contamination inputs to SCH sediment, as they do not originate from point sources that can be easily managed or controlled by federal custodians of SCHs.

The application of source apportionment approaches (as detailed in Chapter 5) is not always a feasible option for NS SCHs, as these approaches can be time consuming and can require large quantities of data to draw meaningful conclusions. Similarly, source apportionment of contaminants, including PAHs, extends outside of the scope of MSSPs. However, the data which is provided by routinely completed MSSPs provides an excellent opportunity for the federal government to evaluate source apportionment of PAHs and other contaminants at a much larger scale (e.g., provincially, or across Canada). The specific application of source apportionment methods as part of SCH management and assessment (outside of the MSSP) would help highlight both potential point source contributions from processes like a spill (e.g., oil spill), property leakage (e.g., oil tank leaks), infrastructure issues (e.g., wharf timbers contributing PAHs from creosote) and estimate non-point sources of PAHs in SCH sediment (e.g., vehicular emissions, biomass combustion). As such, these estimations would support source control and source characterization efforts for SCH sites.

Recommendation: *The vast amount of data produced by the federal DFO-SCH MSSP may prove useful for source apportionment estimations for SCH sediment that occur outside of the scope of the MSSP.*

6.3.6 Temporal Assessment of PAH Sources

Temporal assessment of PAH sources was not completed as part of this study due to data constraints. Therefore, source apportionment estimations relied on an aggregate data set that varied both spatially and over time. As such, is difficult to estimate and distinguish which PAH sources may have historically, or currently, contaminate sediment and if there have been changes in PAH sources over time at the harbour and/or provincial level. This is further complicated as current sediment assessments (MSSPs and ESAs) rely on surficial sediment samples (0-10 cm), while dredging events that regularly occur in NS SCHs can reach the sediment to a depth of 50 cm or greater (Walker et al., 2013a). Dredging events cause contaminants to re-suspend and disperse, making temporal source apportionment approaches difficult to complete with current surficial sediment data. Furthermore, surficial sediment sampling at NS SCHs through the MSSP provides little insight to whether PAHs are the product of current or historical source inputs as routine dredging is so frequently completed. In contrast, sediment cores provide excellent opportunities to delineate contamination inputs over time and would prove useful in attempting to delineate historical and current sources of PAH contamination in SCHs (see Gearing et al., 1991; Buckley et al., 1995; Hoffman et al., 2017). Sediment cores could provide SCH managers with insight that informs both current and future sources (and concentrations) of contamination, leading to better-informed management strategies and federal spending. As such, the adoption of sediment cores as part of a larger assessment of SCHs (outside of the current MSSP), as previously mentioned in section 6.3.5, would support temporal source apportionment estimations for PAHs in sediment.

Recommendation: *Core sampling may prove useful in estimating source apportionment of PAHs in SCHs and to further delineate temporal PAH contamination.*

6.4 STUDY LIMITATIONS

This study demonstrates various limitations which are best organized into the following categories: data-specific limitations, and MSSP-specific limitations.

6.4.1 Data Limitations

As this study hinges on secondary data collected from DFO-SCH, there are certain inherent characteristics of the data that are considered limitations to this study:

- Selected SCHs represent 17.4% of all 178 SCHs in the province of NS. Therefore, these SCHs represent a sub-sample of the greater population and are suggested to be representative. However, this study is not fully comprehensive, as it doesn’t incorporate all SCHs in the province.
- Reports only included parental (non-alkylated) PAH compounds. Alkylated PAHs, which are also present in the environment, were not available for analyses.
- Sediment physicochemical characteristics were not consistently included or assessed across all reports, making completed analyses weaker due to a reduced volume of data.
- Assessment of the temporal variation (increasing/stable/decreasing) of PAHs in SCHs (at the individual harbour or provincial level) could not be completed (e.g., Mann-Kendall Trend) because the sampling intervals for each SCH were not frequent enough.
- SCHs with greater sampling intervals were increasingly impactful in aggregate analyses/calculations, as they contributed an increased number of sediment samples.
- One MSSP report was identified as identical to another report for a different harbour and sampling year. As a precautionary measure, both MSSP reports were discarded from the study and as a result, the number of sediment samples used in analyses decreased somewhat.

- Analytical detection limits (DL) cited in reports resulted in many samples that required censored data approaches (e.g., adopting ½ DL) prior to analysis. This approach is well founded yet reduces the accuracy of the data as it substitutes predetermined PAH concentrations for <DL values that were subsequently used in analyses.
- The transcription and of the PAH concentration data from federal reports into managed documents lends itself to a margin of human error. However, QA/QC efforts (discussed in Chapter 3) sought to minimize the error associated with the data transfer.

6.4.2 MSSP Limitations

The majority of sediment samples analyzed as part of this study were encompassed in MSSP reports (*n*=105) that follow a specific protocol as per the terms of reference (TOR) (Appendix A) defined by DFO-SCH. Therefore, the approach of the MSSP program has the ability to directly influence the data at the core of this study and present certain limitations. In review of MSSPs as part of this study, it was evident that certain aspects of the MSSP protocol may hinder the characterization of PAHs (and other contaminants) in SCH sediment. However, it is important to acknowledge that the MSSP program is completed with a specific purpose and scope, which greatly influences the way it is conducted. Regardless, specific limitations of the MSSP that may impair PAH characterization in SCHs include: sediment sampling design, the number of sediment samples, and the lack of reference sampling.

6.4.2.1 Sediment Sampling Design

The MSSP focuses sediment sampling specifically to the dredging area of the harbour and employs a random grid design. This sampling design is considered a biased sampling design, as it focuses on the proposed dredging area only (CCME, 2016). This sampling design lends itself to a smaller number of samples being required (CCME, 2016). It is important to note that given the likely ongoing inputs to working SCH environments, it is very unlikely that sediment contamination by PAHs occurs solely within the proposed dredging area (FCSAP, 2017). As such, PAH contamination may not be accurately characterized for the entire SCH by the current MSSP sediment sampling design.

Unbiased sampling (randomly taken across an entire site) would ultimately support a stronger and more accurate representation of PAHs across the entire SCH site and have greater utility in terms of statistical analyses and comparisons to reference samples (CCME, 2016). In the context of risk assessment, a mixture of biased and unbiased sampling methods is suggested to be the strongest sediment sampling design to best assess a site (CCME, 2016). Therefore, the MSSP sampling design should encompass both biased and unbiased sampling approaches, which would improve the characterization and assessment of PAHs (and other contaminants) in SCHs.

Recommendation: *The MSSP sampling design should encompass both biased and unbiased sampling approaches, which would improve the characterization and assessment of PAHs (and other contaminants) in SCHs.*

6.4.2.2 Number of Sediment Samples

MSSP reports vary in the number of sediment samples which are assessed. Sampling is completed as per the Environment Canada *Guidance Document on Collection and Preparation of Sediments for Physicochemical Characterization and Biological Testing* (1994) which highlights that in most cases, 1-5 discrete sediment samples can be used to assess sediment (Environment Canada, 1994). This consideration is heavily influenced by the cost of sampling and the specific objective(s) of the MSSP (PSPC, 2014; CCME, 2016). Upon review of 105 MSSPs, most reports contain between 3 and 6 sediment samples, which may be inadequate to best characterize PAHs at SCHs, especially if SCHs are large in area.

Generally speaking, sediment sample numbers are often difficult to determine in any project, including MSSPs, as they must be decided on in the context of environmental objectives, site specific considerations, and financial constraints (Alvarez-Guerra et al., 2009; Paladino et al., 2014; CCME, 2016). CCME Guidance [Manual for Environmental

Site Characterization in Support of Environmental and Human Health Risk Assessment (2016)], indicates that *"a common pitfall of site investigations is the collection of too few sediment samples"* (CCME, 2016). However, with environmental protection in mind, a greater number of sediment samples will help to provide the most accurate and representative results for PAHs and other contaminants in SCHs (Walker et al., 2013a; CCME, 2016). To boost the number of samples collected as part of MSSPs, composite sampling (gathering many samples and taking a subsample of the aggregate) could be explored as an option to improve sampling efforts, as it maintains low analytical costs, while potentially covering a larger sampling area (Walker et al., 2013a).

Recommendation: *To best characterize PAHs (and other contaminants), a greater number of sediment samples should be taken at each SCH site, within the budget of the MSSP.*

6.4.2.3 Lack of Reference Sampling

The MSSP approach does not currently assess sediment data with reference samples (samples which are taken from similar sites for comparison) in mind. This is not surprising given that the objective of the program is to dispose of dredged sediment and is less concerned with ecological and/or human health risks of the sediment currently residing in the aquatic environment. This approach encourages comparisons to environmental quality guidelines that are focused solely on sediment disposal. However, reference sampling is very important when interpreting sediment quality data, especially when completing statistical comparisons, and could prove useful for federal custodians when evaluating MSSP reports (Krantzberg et al., 2000; CCME, 2016). Specific to PAHs, the ubiquity and persistence of these compounds, coupled with the fact that they can be produced naturally, are two key considerations that further support reference sampling as a valuable tool to aid interpretation of PAH data from MSSPs. Reference sampling can support prioritization efforts for SCHs as it would help to identify those which are extremely contaminated by PAHs (or other contaminants), or SCHs which have site-specific PAH issues. Similarly, if data derived from the MSSP program is to serve any risk assessment purposes in the future, it is crucial that reference sampling occurs as it can help delineate site-specific contamination and distinguish such contamination from that which is attributed to off-site or ambient contamination sources.

Recommendation: *DFO-SCH should consider gathering reference samples from aquatic sites which mimic SCH environments, as reference sampling demonstrates utility in interpreting data collected for MSSP reports.*

6.5 RECOMMENDATIONS FOR FUTURE RESEARCH

The ubiquity and persistence of PAH compounds, coupled with the importance of SCH environments in the province of NS, warrants additional investigation into the assessment and source apportionment of PAHs. An expanded study that evaluates all SCHs in NS would be increasingly comprehensive and provide a stronger indication of PAH distributions and potential PAH sources. Furthermore, a study which evaluates PAHs over a greater temporal period would demonstrate utility in addressing potential changes in PAHs across SCHs over time. Further examination of sediment physicochemical characteristics and the relationship these characteristics have to PAHs would be extremely useful in best understanding how sediment characteristics may influence PAH behaviour in SCHs, and the implications of these relationships for SCH management. Specifically, the following recommendations for future research include:

- A similar study that examines PAH assessment and source apportionment across all 178 NS SCHs.
- A comparative study that seeks to estimate PAH source apportionment by different lines of evidence, including the potential application of principal component analysis, positive matrix factorization, and other approaches, as appropriate.
- Case study research that examines NS SCHs most contaminated by PAHs (Canso, Fox Point) and that seeks to delineate PAHs in these environments.

- A study that investigates the importance of physicochemical sediment characteristics in NS SCHs and how these characteristics influence hydrophobic contaminants, including PAHs.
- A comparative study of PAH assessment and source apportionment for SCH sediments across all Atlantic provinces (NS, NB, PE, NL).
- A comparative study of PAH assessment and source apportionment for SCH sediments across all DFO-SCH management regions in Canada.
- A study that investigates the biological implications of PAHs in NS SCH sediments by various biological toxicity evaluations/assays.

6.6 CONCLUDING COMMENTS

This research has gathered information that supports the characterization and assessment of PAHs in NS SCH sediments. The evidence provided as part of this study demonstrates utility for SCH managers within the NS context and beyond, by holistically analyzing primary MSSP data collected by the federal government. As environmental protection efforts continue to progress, greater value is being placed on managing contaminants that are the result of anthropogenic activities and that have the ability to negatively impair aquatic environments, which includes ubiquitous PAHs. As such, source apportionment approaches and improved characterization and assessment of contaminants will continue to be valuable tools that support environmental management of SCHs in NS and beyond. In support of these efforts, publicly available federal aggregate data may present a unique opportunity to better understand anthropogenic contaminants, their origin(s), and their behaviour in the environment.

Acknowledgements: This work was supported by NSERC Discovery Grant RGPIN-2018-04119 to T.R.W.

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APPENDIX A
DFO-SCH Terms of Reference (TOR) For Marine Sediment Sampling Program (MSSP)

TERMS OF

REFERENCE

FOR

MARINE SEDIMENT SAMPLING
PROGRAM (MSSP)

AT

Cape St. Marys Small Craft

Harbour for

Fisheries and Oceans Canada – Small Craft Harbours
Branch

Prepared by

Public Works & Government Services
Canada Environmental Services

May 6, 2014

1.0 INTRODUCTION

Public Works and Government Services Canada (PWGSC), is initiating work to perform a Marine Sediment Sampling Program (MSSP) at Cape St. Marys SCH. The Harbour Code is 1046.

2.0 SCOPE OF WORK

The scope of work includes the following:

I. Preparation and collection of marine sediment samples to be analyzed and compared against applicable guidelines.

   The requirements for the sampling program include the following:

   1. The dredge area is identified in separately provided pdf and AutoCAD plans. The anticipated dredge volume is 5000 cubic meters place measure.

   2. Based on the proposed dredge area and volume, six (6) are to be collected and analyzed.

      Additional (back-up) samples will be collected at each location and stored until the completion of the sediment sampling program (PWGSC Project Manager must provide approval to dispose/destroy samples).

   3. The marine sediment sampling locations will be selected by creating a numbered grid of at least thirty (30) cells that are spatially representative of the dredge area. A random number generator should be employed generating random numbers selected from one (1) to at least thirty (30). The random numbers generated will be representative of the numbered cells of the grid and subsequently the sample locations.

      The draft sampling plan (figure showing proposed sample locations, coordinates and whether samples are surface/sub-surface) will be submitted and approved by the PWGSC Project Manager. Approval of the sampling plan by the PWGSC Project Manager is required prior to any fieldwork.

   4. The document *"Guidance Document on Collection and Preparation of Sediments for Physiochemical Characterization and Biological Testing, Environment Canada, December 1994"* is to provide overall guidance on the method, handling and transportation of marine sediment samples.

      Specific section references include:

- Section 2.5 (Collection of Whole Sediments)
- Section 2.7 (Handling of Collected Samples); and
- Section 2.8 (Transport and Storage of Field-collected Sediments)

<u>*Please note:</u> Specific details indicated here in the TOR will supersede guidance in the EC document.

5. The samples to be collected will be surface (grab).

6. Sample locations will be verified in the field utilizing Global Positioning System (GPS) Coordinates Lat/Long and UTM (NAD 83).

   <u>*Please note:</u> While maps and possibly georeferenced maps will be provided to the consultant, PWGSC cannot confirm their accuracy as the maps are obtained from various sources. The consultant must ensure that the coordinates for the MSSP are correct.

7. Samples are to be analyzed by an accredited laboratory with CALA and/or ISO/IEC 17025 and are certified by the Standards Council of Canada (SCC) for each select chemical analyses.

8. Silica Gel clean up will be required for all samples analyzed for Petroleum Hydrocarbons.

9. Marine samples are to be analyzed for the following parameters:

a) **TPH and BTEX**
Low level analysis for BTEX to allow comparison to CCME SQGs. A return to baseline at C32 is required and is to be verified.

b) **Polycyclic Aromatic Hydrocarbons (PAHs)**
Low level analysis for new 2010 CCME guidelines and inclusion of a scan for creosote.

c) **Metals**
ICP 23 Metals scan plus mercury and hexavalent chromium

d) **Polychlorinated Biphenyls (PCBs) and DDT suite**

e) **Carbon Content (TIC and TOC)**

f) **Grain Size Distribution**

g) **Leachate** [as required (i.e. Nova Scotia for PAHs, Metals, etc]

- SPLP (Synthetic Precipitation Leaching Procedure) Leachate (EPA 1312 methodology) for potential land based disposal.

Please note: Leachate analysis for selected parameters will be determined in conjunction with PWGSC upon receipt of sample results and will only be performed for parameters exceeding applicable guidelines. **Assume minimum two (2) leachate samples to be analyzed for each applicable parameter (PAH leachate and Metal leachate).**

10. Analytical costs to be based on standard turnaround time. Laboratory results are to be compared against the following applicable guidelines:

    - Atlantic RBCA Version 2.0 Tier I Risk Based Screening Levels
    - CCME Soil Quality Guidelines (SQGs)
    - CEPA Ocean Disposal Guidelines (ODG)
    - For leachate: Canadian Drinking Water Quality Guidelines (CDWQG) and CCME Water Quality Guidelines (WQGs)

    The following guidelines are included in the Appendix B table(s) of the report, however no comparison in the body of the report is required:

    - CCME Sediment Quality Guidelines (Interim Sediment Quality Guidelines (ISQGs)
    - CCME Sediment Quality Guidelines (Marine and Estuarine Probable Effects Levels (PELs)

II. Preparation of a draft report for review by PWGSC. The draft report complete with appendices) is to be provided by email to PWGSC (one (1) pdf file).

III. Incorporation of comments received by PWGSC.

IV. Preparation of a final report provided to PWGSC. The final report is to be provided to PWGSC (one (1) pdf file by email); and two (2) hardcopies of the report and one (1) digital CD version (pdf file) provided by mail (in unsecure pdf format).

V. Laboratory results will also be provided by email in a separate electronic file that meets Environment Canada (EC) format for transfer to GIS as per the excel template "EnvCan - Disp. at Sea GIS Export format" which will be provided upon request.

3.0 PROJECT MANAGEMENT

Budget and Schedule Control

No work shall be undertaken which is additional or supplemental to or in substitution of the work and budget specified, unless approved in writing in advance.

The Consultant shall maintain the project schedule that is agreed upon with the PWGSC Project Manager at the project initiation. The schedule will be in accordance with the project Gantt chart enclosed in the Consultant's proposal submission, as well as any necessary modifications agreed upon with the PWGSC Project Manager. Any revised schedules shall be submitted to the PWGSC Project Manager.

The Consultant shall also provide a status update (by email) at a minimum of every 2 (two) weeks to the PWGSC Project Manager advising of the project status. However, any critical changes to scope of work, budget or schedule should be reported to the PWGSC Project Manager as soon as possible.

4.0 HEALTH AND SAFETY

Upon acceptance of the cost proposal, the Consultant must provide a site-specific Health and Safety Plan (HASP) and submit it to the PWGSC Project Manager prior to the commencement of any field work.

It is the Consultant's responsibility to be familiar with and conform to all applicable Safety Acts, Regulations, Codes and contract requirements.

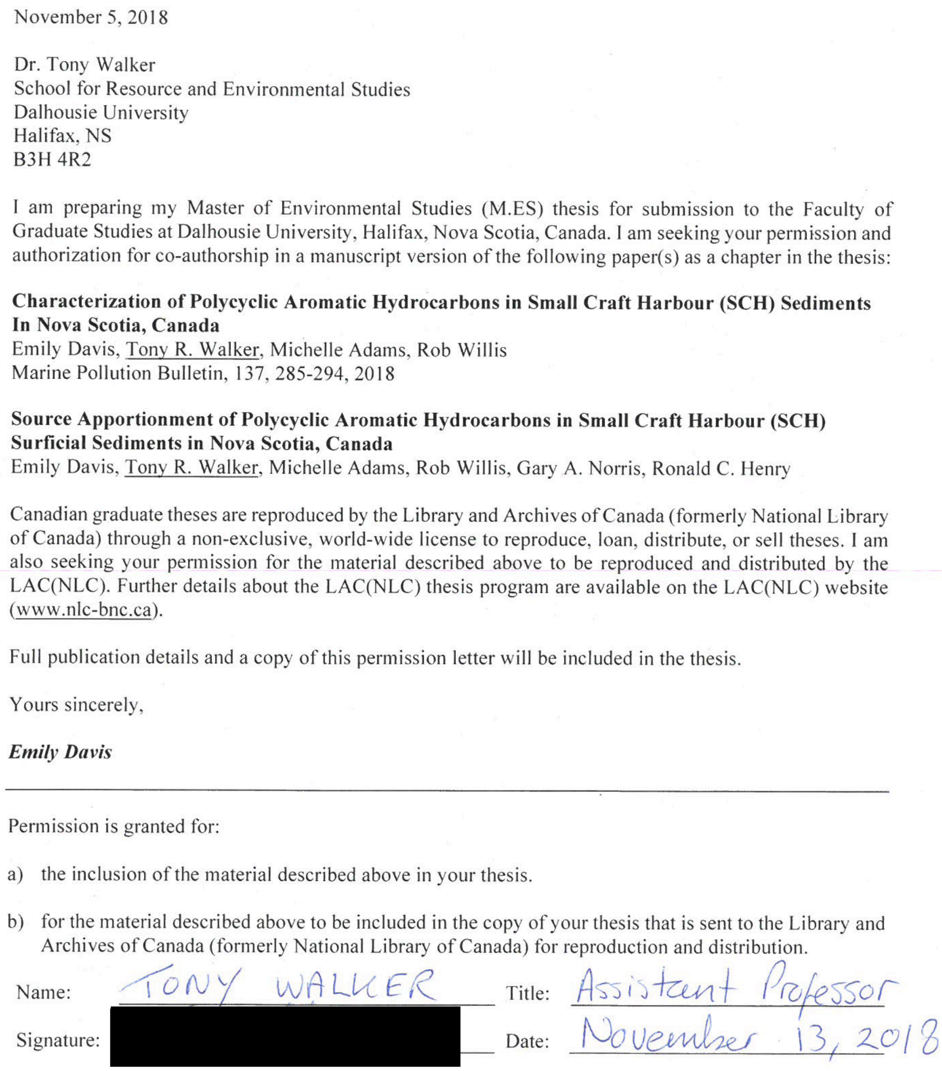
The Consultant shall ensure that all workers and authorized persons entering the work site are notified of and abide by the site-specific HASP, safety rules, procedures, safe work practices and applicable Safety Acts, Regulations, and Codes. Any persons not complying with the applicable Acts, Regulations, Codes, or the Health and Safety Plan shall not be permitted on the site.

***Please note**: Acceptance of the site-specific HASP by PWGSC shall only be viewed as acknowledgment that the Consultant has submitted a plan. PWGSC makes no representation and provides no warranty for the accuracy, completeness and legislative compliance of the plan by its acceptance.

APPENDIX B
Report and Sampling Interval Information for 31 SCHs Selected

Harbour	Region	Reports	Years Sampled
Arisaig	Gulf	4	2004, 2005, 2009, 2016
Baileys Brook	Gulf	10	2004, 2005, 2009, 2010 (2), 2011 (2), 2012, 2013, 2017
Barrios Beach Tracadie	Gulf	2	2001, 2009
Caribou Ferry	Gulf	4	2005 (2), 2009, 2013
Inverness	Gulf	6	2003, 2007 (2), 2009, 2010, 2014
Judique (Baxters Cove)	Gulf	6	2004, 2008, 2010 (2), 2012, 2014
Pictou Landing	Gulf	3	2005, 2007, 2013
Pleasant Bay	Gulf	4	2004, 2007, 2010, 2014
Skinners Cove	Gulf	6	2004, 2007, 2009 (2), 2010, 2014
Canso	Eastern	2	2004, 2008
Glace Bay	Eastern	4	2007, 2010 (2), 2012
Neils Harbour	Eastern	2	2008, 2009
Owls Head	Eastern	5	2007, 2008, 2010 (2), 2015
Port Morien	Eastern	3	2004, 2009, 2010
Three Fathom Harbour	Eastern	3	2009, 2010, 2012
Centreville	Southwest	3	2004, 2008, 2009
Hunts Point	Southwest	4	2005, 2009, 2010, 2012
Little Harbour Shelburne	Southwest	3	2006, 2009, 2017
Little River Yarmouth	Southwest	2	2009, 2013
Moose Harbour	Southwest	4	2003, 2008, 2009, 2015
Pinkney's Point	Southwest	3	2005, 2013, 2015
South Side	Southwest	2	2005, 2013
Stoney Island	Southwest	4	2006, 2009, 2010, 2015
Yarmouth Bar	Southwest	3	2006, 2010, 2015
Battery Point	Southwest	3	2006, 2009, 2013
Clarks Harbour	Southwest	2	2003, 2006
Delaps Cove	Southwest	4	2006, 2009, 2013, 2017
Fox Point	Southwest	2	2005, 2006
Hampton	Southwest	6	2003, 2007, 2008, 2009, 2012, 2016
Sandford	Southwest	4	2004, 2006, 2008, 2013
Westport	Southwest	2	2009 (2)

Appendix C
Copyright Agreement Letters for Co-Authorship



November 5, 2018

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

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

Characterization of Polycyclic Aromatic Hydrocarbons in Small Craft Harbour (SCH) Sediments In Nova Scotia, Canada
Emily Davis, Tony R. Walker, Michelle Adams, Rob Willis
Marine Pollution Bulletin, 137, 285-294, 2018

Source Apportionment of Polycyclic Aromatic Hydrocarbons in Small Craft Harbour (SCH) Surficial Sediments in Nova Scotia, Canada
Emily Davis, Tony R. Walker, Michelle Adams, Rob Willis, Gary A. Norris, Ronald C. Henry

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Yours sincerely,

Emily Davis

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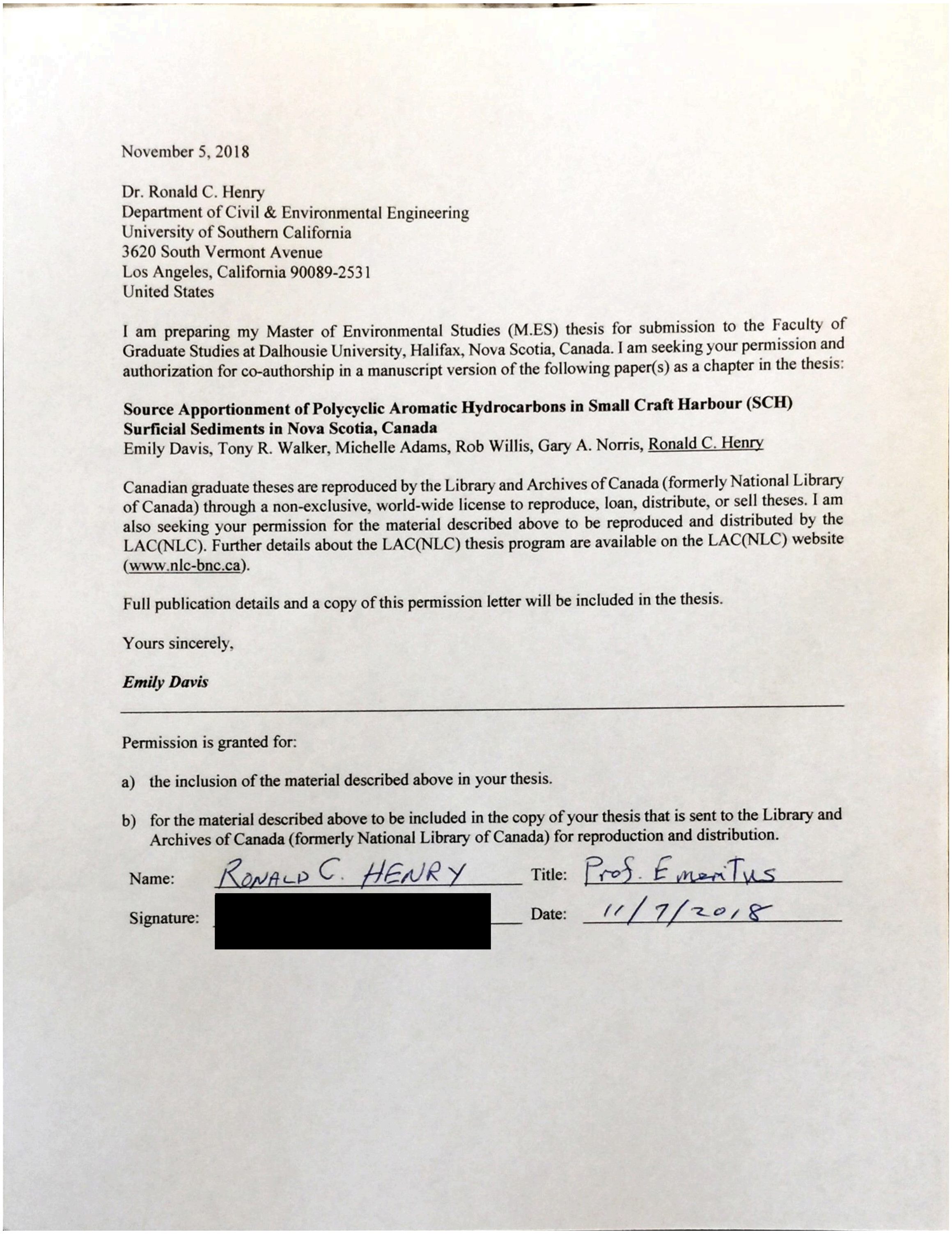
Name: TONY WALKER Title: Assistent Professor

Signature: [redacted] Date: November 13, 2018



November 5, 2018

Dr. Ronald C. Henry
Department of Civil & Environmental Engineering
University of Southern California
3620 South Vermont Avenue
Los Angeles, California 90089-2531
United States

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Name: RONALD C. HENRY Title: Prof. Emeritus

Signature: [redacted] Date: 11/7/2018

November 5, 2018

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

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

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Name: Rob Willis Title: Sr. Toxicologist

Signature: [redacted] Date: Nov 14, 2018

November 5, 2018

Dr. Michelle Adams
School for Resource and Environmental Studies
Dalhousie University
Halifax, NS
B3H 4R2

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Emily Davis

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Name: Dr. Michelle Adams
Title: Associate Professor
Signature: [redacted]
Date: November 9th, 2018

November 5, 2018

Dr. Gary A. Norris
US EPA, Office of Research and Development
Research Triangle Park, North Carolina 27709
United States

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

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Emily Davis

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Name: Gary Norris Title: Scientist

Signature: [redacted] Date: 11/6/18