IDENTIFYING LAKE WATER QUALITY TRENDS AND EFFECTIVE MONITORING STRATEGIES IN A RAPIDLY URBANIZING REGION

by

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Dalhousie University is located in Mi'kma'ki,

the ancestral and unceded territory of the Mi'kmaq.

We are all Treaty people.

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ABSTRACT

Water quality degradation in freshwater lakes is widely observed and largely attributed to human activities, particularly in urban regions. The city of Halifax, NS, is among the fastest growing urban centers in Canada, potentially threatening the health of surrounding waterbodies. This thesis analyzed water quality trends in a set of ~50 lakes that have been sampled on a decadal-basis over a 40-year period in the Halifax Regional Municipality (HRM). Trophic state was also tracked in a subset of lakes over the 2021 open-water season to evaluate common and novel strategies for monitoring lake health. Aluminum, chloride, manganese, and arsenic concentrations were found to exceed national guidelines for the protection of aquatic life in one or more of the study lakes in 2021. Urban development was identified as an important driver of increasing chloride, conductivity, sodium, calcium, and total phosphorus (TP) concentrations. Regional factors, including climate change and decreasing acid deposition, hydrology, and watershed characteristics are believed to be stronger drivers of other observed changes. Decadal spring synoptic surface sampling was determined to be useful at highlighting emerging water quality concerns but may be less effective at characterizing parameters that are more spatially and temporally variable, such as nutrients, particularly in lakes where internal P loading occurs. More rigorous sampling is required to accurately characterize nutrient dynamics, and parameters that appear to be influencing trophic state (e.g., color, and chloride and DOC concentrations) require further exploration. Research findings support the continued use of TP as a trophic state indicator and demonstrated that the TP-chlorophyll *a* relationship identified by the Organization for Economic Cooperation and Development (OECD) Cooperative Programme on Eutrophication in the 1970s remains applicable in HRM lakes despite changes in climate and varied lake and watershed characteristics. This thesis contains baseline data for lake water quality in HRM which will inform future lake management efforts and highlights water quality concerns that should be the target of monitoring efforts in the broader context of temperate urban lakes.

LIST OF ABBREVIATIONS AND SYMBOLS USED

%	Percent
[H^+]	Hydrogen ion molar concentration
Δ	Delta or "change in"
°C	Degrees Celsius
AIC	Akaike information criterion
BC MECCS	British Columbia Ministry of Environment and Climate Change Strategy
$CaCO_3$	Calcium carbonate
CCME	Canadian Council of Ministers of the Environment
Chl *a*	Chlorophyll *a*
cm	Centimeter
CWRS	Centre for Water Resources Studies
DEM	Digital elevation model
dev_1980	Proportion of watershed developed in ~1980
dev_2020	Proportion of watershed occupied by development in 2020
dev_change	Change in proportion of watershed developed from ~1980 to 2020
DO	Dissolved oxygen
DOC	Dissolved organic carbon
ECCC	Environment and Climate Change Canada
flush_proxy	Total watershed area / lake surface area (flushing rate proxy)
g	Gram
HAB	Harmful algal bloom
HRM	Halifax Regional Municipality
HRMOD	Halifax Regional Municipality Open Data
ISODATA	Iterative Self-Organizing Data Analysis Techniques
km	Kilometer
km^2	Square kilometer
L	Liter
m	Meter
m^2	Square meter
m^3	Cubic meter
max_depth	Lake maximum depth (m)
mg	Milligram
mL	Milliliter
NSDNRR	Nova Scotia Department of Natural Resources and Renewables
NSECCU	Nova Scotia Environment – Climate Change Unit
OECD	Organization for Economic Cooperation and Development
OLI	Operational Land Imager
P	Phosphorus
PC	Principal component
PCA	Principal component analysis
R^2	Coefficient of determination

road_density	Road density within watershed (km/km^2)
surface_area	Lake surface area (km^2)
TCU	Total color units
TIN	Triangulated irregular network
TM	Thematic Mapper sensor
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TP_{epi}	Arithmetic mean TP concentration in the epilimnion
TP_{hyp}	Arithmetic mean TP concentration in the hypolimnion
TP_{pz}	Arithmetic mean TP concentration in the photic zone
TP_{syn}	Synoptic spring surface sample TP concentration
TP_{vw}	Volume-weighted TP concentration for entire lake basin
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
volume	Estimated lake volume (m^3)
watershed	Watershed area (km^2)
wetland	Proportion of watershed occupied by wetlands
WWTF	Wastewater treatment facilities
μg	Microgram
μm	Micrometer
μS	Microsiemen
χ^2	Chi-square

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This research focuses on a set of lakes that are located within Mi'kma'ki, the ancestral and unceded territory of the Mi'kmaq. The Mi'kmaw names of several study lakes can be found in the Ta'n Weji-sqalia'tiek Mi'kmaw Place Names Digital Atlas and Website Project (mikmawplacenames.ca) and are included in Table A.1. I am grateful to have had the opportunity to conduct research within Mi'kma'ki and recognize my responsibility to work toward reconciliation and the protection and preservation of this land for future generations.

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CHAPTER 1 – INTRODUCTION

1.1 Anthropogenic and natural factors influencing lake water quality

Surface waters, particularly those within proximity to urban centers, are susceptible to degradation arising from anthropogenic activities. Various contaminants are associated with human activities (e.g., major ions, nutrients, fecal pathogens, trace elements and heavy metals, plastics, etc.) and can reach surface waters through direct and indirect pathways (Howell et al. 2012; Ren et al. 2014; Stea et al. 2015; Dugan et al. 2017; Scott et al. 2019). These contaminants may be delivered by point sources, such as wastewater and stormwater effluent, or diffuse inputs, including atmospheric transport of industrial emissions, surface runoff, and groundwater discharge. Vast disturbances are caused by urban development, agriculture, and resource extraction activities, exposing soils and bedrock to increased weathering and thus mobilizing contaminants. The vegetation removal and increased impervious surface coverage associated with these disturbances alters watershed hydrology, both by decreasing the retention of contaminants (e.g., nutrients) within the watershed and increasing surface runoff, thus accelerating the delivery of sediments and contaminants to downstream surface waters (Hall et al. 1999).

The widespread increases in lake salinity observed across temperate regions, primarily attributed to the runoff of road de-icing salt, clearly illustrate the potential for contaminants of anthropogenic origin to reach and negatively affect surface waters (Novotny and Stefan 2012; Dugan et al. 2017; Scott et al. 2019). Increasing chloride ion concentrations often exceed toxicity thresholds, particularly in urban regions, and have the potential to alter the physical, chemical, and biological processes within lake ecosystems (Novotny and Stefan 2012; Kilgour et al. 2013; Dugan et al. 2017; Scott et al. 2019). Direct toxic effects to organisms have been observed in the short- and long-term, and include limiting growth and reproduction, which can dramatically alter community structure and decrease biodiversity (CCME 2011; Hintz et al. 2017; Dugan et al. 2017). In addition to the direct toxic effects to biota, increased chloride concentrations alter lake mixing regimes by reinforcing stratification which can exacerbate the depletion of dissolved oxygen (DO) within the hypolimnion and thereby create conditions that favor the release of stored phosphorus (P) and other mobile contaminants (e.g., arsenic) from sediments (Novotny and Stefan 2012).

Increased nutrient loading is another adverse effect associated with proximity to urban centers and is responsible for the rise in eutrophication observed globally (Vollenweider and Kerekes 1982; Schindler and Vallentyne 2008). Eutrophication refers to increased primary productivity within freshwaters and is largely attributed to increased P loading (Schindler et al. 1973; Vollenweider and Kerekes 1982). Lake P concentrations are influenced by both external and internal P loading (Sharpley et al. 1994; Nürnberg 2009). External sources of P include wastewater and stormwater effluent, surface run off containing fertilizers, and discharge from residential septic systems (Cullen and Forsberg 1988; Sharpley et al. 1994; Moore et al. 2003; McCray et al. 2005). Internal P loading is enabled by anoxic conditions in the hypolimnion favoring the release of stored P from sediments into the water column (Nürnberg 2009). Unlike constituents that have primary toxic effects to organisms, the detrimental effects of increasing P concentrations to aquatic life are a result of its secondary effects, including eutrophication and, by extension, anoxic conditions that have resulted in fish kills, loss of habitat, and shifts in community structure (CCME 2004; Chislock et al. 2013; Carmichael and Boyer 2016). Further, eutrophication has the potential to create a positive feedback loop as it exacerbates the depletion of hypolimnetic DO concentrations and thus increases internal P loading (Correll 1998; Nürnberg 2009; Chen et al. 2018). Eutrophic conditions are also associated with reduced water clarity, and the release of toxins by harmful algal blooms (HABs) (Moore et al. 2008; Paerl et al. 2011; Chislock et al. 2013; Pick 2016; Chapra et al. 2017).

In some regions, surface water warming associated with anthropogenic climate change, rather than increased external nutrient loading, has been identified as the primary driver of eutrophication (Summers et al. 2016). Increasing surface water temperatures alter lake ice cover duration and reenforce hypolimnetic anoxia by strengthening and prolonging thermal stratification (Moore et al. 2008; Nürnberg 2009; Paerl et al. 2011; Woolway et al. 2020). This, in turn, facilitates internal nutrient loading, thus contributing to eutrophication risk (Moore et al. 2008; Nürnberg 2009; Paerl et al. 2011). Further, climate change has been identified as a driver of the observed shift from benign algal blooms to HABs by creating favorable conditions for cyanobacteria which, at times, release toxins that are harmful or even lethal to various organisms, including humans (Moore et al. 2008; Paerl et al. 2011; Pick 2016; Chapra et al. 2017). In addition to surface water warming, the increasing air temperatures and increased frequency of extreme weather events associated with climate change mobilize constituents such as dissolved organic carbon (DOC), iron, and nutrients from within watersheds (Harrison et al. 2008; Sarkkola et al. 2013).

While climate change is partly responsible for the widespread increases in lake DOC concentrations that have been observed in recent years, decreasing acid deposition is another likely driver (Redden et al. 2021). Prior to the implementation of emission control policies throughout the 1980s and 90s, industrial emissions of sulfur oxides, such as those emitted by power generating plants, led to widespread atmospheric acid deposition, altering the chemistry of surface waters throughout North America and threatening the health of ecosystems (Schofield 1976; Clair et al. 2011). Within lake ecosystems, acid deposition resulted in increased sulphate concentrations and decreased pH, alkalinity, DOC, and calcium concentrations, with the most pronounced effects observed in regions having little buffering capacity. Legacy effects from acidification have persisted decades beyond the implementation of emissions controls (Clair et al. 2011; Redden et al. 2021). In recent years, signs of chemical recovery have been inconsistent, with increases observed in DOC concentrations, pH, and alkalinity, while base cations (i.e., calcium) continue to decline, likely due to their depletion in the soils (Clair et al. 2011; Redden et al. 2021).

Assessing a lake's vulnerability to the stressors posed by urban influence and predicting the efficacy of lake management efforts is further complicated by the watershed characteristics and various morphological, hydrological, and physical factors that influence lake water chemistry. Dominant vegetation types, watershed soil and bedrock composition, and the presence and size of organic matter stores, such as those found in wetlands, all influence lake water quality, including pH, color, DOC concentration, nutrients, major ions, and trace elements (Gorham et al. 1986; Gergel et al. 1999;

McDonald et al. 2004; Clair et al. 2011). Flushing rate—which can be approximated by comparing lake surface area to watershed area—affects both contaminant loading potential and contaminant residence time (Gorham et al. 1986; George and Hurley 2003; Jones et al. 2008). As a result, higher flushing rates are associated with decreased eutrophication risk (Kerekes 1975; Jones and Elliott 2007; Londe et al. 2016; Hoyer and Canfield 2022).

Lake productivity dynamics, and, by extension, eutrophication risk, are also influenced by various physical and chemical factors, including mean depth, surface area, and wind exposure (e.g., fetch), which influence lake stratification potential, and by extension, the cycling of constituents within the lake water body and internal P loading potential (Spears et al. 2013; Grzybowski 2014; Quinlan et al. 2021; Hoyer and Canfield 2022). As previously mentioned, chloride concentration is capable of influencing lake productivity dynamics due to the toxic effects of chloride on primary producers and resulting shifts in community structure, as well as the reinforcement of stratification and thus exacerbation of internal P loading (Novotny and Stefan 2012; Hintz et al. 2017; Dugan et al. 2017; Fournier et al. 2021; Radosavljevic et al. 2022; Hébert et al. n.d.).

The widespread observed increases in DOC and color observed throughout the northern hemisphere, termed “lake brownification” or “browning,” have a highly variable relationship with lake productivity (Carpenter et al. 1998; Grzybowski 2014; Fergus et al. 2016; Hoyer and Canfield 2022; Tammeorg et al. 2022). At times, DOC and color have been found to suppress productivity, largely by limiting light availability and reducing the rate of internal P loading due to the binding of humic substances to P in the hypolimnion (Jones et al. 1988; Jones 1992; Carpenter et al. 1998; Carvalho et al. 2011; Thrane et al. 2014; Vuorio et al. 2020; Stetler et al. 2021; Hoyer and Canfield 2022; Tammeorg et al. 2022), while a positive relationship with productivity has been observed in other studies (Fergus et al. 2016; Senar et al. 2021; Tammeorg et al. 2022). Nutrients bound to DOC may partly explain this phenomenon, as well as UV protection to algal cells at low DOC concentrations and temperature increases associated with light attenuation (Carpenter et al. 1998; Senar et al. 2021; Isles et al. 2021; Fonseca et al. 2022; Puts et al. n.d.).

1.2 Water quality monitoring and lake management

The emerging water quality concerns in lakes around the globe associated with urban development and anthropogenic activities underscore the importance of comprehensive monitoring strategies and effective lake management. This includes establishing baseline conditions so that changes can be quantified and, when possible, identifying key drivers of observed changes.

National guidelines for the protection of aquatic life, as per the Canadian Council of Ministers of the Environment (CCME), identify thresholds at which toxic effects may occur in aquatic life and thus provide an invaluable resource for the protection of lake ecosystems. Thresholds for both short- and long-term exposure are often recognized that aim to protect the most sensitive life stages of organisms. Often, thresholds are not fixed concentrations, and are instead influenced by various toxicity modifying factors, including pH, hardness, and DOC concentration (CCME 2019). At times however, national guidelines may fail to provide adequate protection, such as in the case of chloride ion concentrations (Hintz et al. 2022).

Increasing concern regarding eutrophication risk in the 1960s led to the initiation of the Organization for Economic Cooperation and Development (OECD) Cooperative Programme on Eutrophication which characterized relationships between nutrients and productivity to develop trophic state models that continue to inform lake eutrophication management strategies decades later (Vollenweider and Kerekes 1982). Data was collected from temperate, eutrophic lakes around the world and P was identified as the primary driver of lake productivity and an effective trophic state indicator (Vollenweider and Kerekes 1982). In 1981, these findings were evaluated in lakes across Canada (largely oligotrophic and located in undeveloped areas) and the statistical relationships observed were largely deemed to conform with those identified in the original OECD study lakes (Janus and Vollenweider 1981). A notable amendment made to the OECD's original trophic state classification system for Canadian lakes was the subdivision of the "meso-eutrophic" category into "mesotrophic" and "meso-eutrophic" categories to account for the variety of Canadian lakes falling within these categories (CCME 2004) (Table B.1). These categories are dictated by total phosphorus (TP) rather than Chl *a* concentrations (a more direct measure of productivity) due to the comparable ease with which the former parameter can be measured (Cloutier and Sanchez 2007; Pasztaleniec 2016).

It should be noted that various factors may influence nutrient-productivity dynamics which could alter the reliability of the OECD relationships. This includes chemical factors such as nutrient availability, pH, and alkalinity, as well as physical factors such as elevation, temperature, mean depth, and light penetration (Spears et al. 2013; Quinlan et al. 2021; Hoyer and Canfield 2022). Spears et al. (2013) suggested that these factors may influence the reliability of TP as an indicator of productivity at a lake-specific scale and, in such cases, P load reduction will be less effective than expected at limiting eutrophication. Further, Quinlan et al. (2021) found that many physical characteristics affect the linearity of the TP-Chl *a* relationship, making it difficult to estimate Chl *a* based solely on TP concentration. Additionally, they assert that while a linear relationship adequately characterizes the TP-Chl *a* relationship at intermediate TP concentrations (4 to 230 ug/L), non-linear relationships might be more appropriate for characterizing the relationship between the two parameters at either extremely low or extremely high TP concentrations (Quinlan et al. 2021). This uncertainty regarding the applicability of the OECD relationship given diverse physical and chemical conditions underscores the need for further exploration of the applicability of the results to understudied lakes, and regions experiencing environmental change.

1.2.1 Lake management in the Halifax Regional Municipality

The Halifax Regional Municipality (HRM) in Nova Scotia, Canada, is home to over 1,000 lakes that are of great ecological, cultural, and economic value. In addition to their environmental importance, HRM's lakes offer their aesthetic value, support tourism, increase property value, provide opportunities for recreational activities, and several are relied upon for drinking water. As the largest municipality in Atlantic Canada, HRM supports a population of over 400,000, and is recognized as one of the fastest growing cities in Canada (Statistics Canada 2021; Statistics Canada 2022). Due to the threats posed by urban development to surface waters, the importance of lake management and water quality monitoring within the municipality is apparent. Research in the region has revealed that road salt, fecal pathogens, nutrients, acid precipitation, heavy metals, silt, invasive species, and climate change are among the issues that threaten the health of lake ecosystems in HRM (Darbyshire and Francis 2008; Stea et al. 2015; Ginn et al. 2015; Clement and Gordon 2019; LeBlanc et al. 2020; Clark et al. 2021).

In 1980, the Synoptic Water Quality Study (SWQS) of select HRM lakes was initiated to create a database of regional lake water quality and to monitor changes over broad time scales (Clement and Gordon 2019). The surveys measure standard water quality parameters (e.g., major ions, nutrients, pH, organic matter, and trace elements) in ~50 lakes on a decadal basis (1980, 1991, 2000, 2011, 2021) and involve the cooperation of federal, provincial, and academic partners (Clement and Gordon 2019). The synoptic approach involves the collection of numerous samples over a short period of time—typically within the span of a single day to reduce temporal variability. This is achieved by collecting samples from a helicopter for most lakes and using boats for lakes that are inaccessible by helicopter. Spatial variability in water chemistry within the lakes is minimized by sampling during spring turnover, immediately following ice-out. The lakes were selected from locations across the municipality to capture the diversity of morphological and watershed characteristics present in HRM lakes, as well as varying degrees of exposure to urban development, and are illustrated in Figure 1.1 (Table A.1).

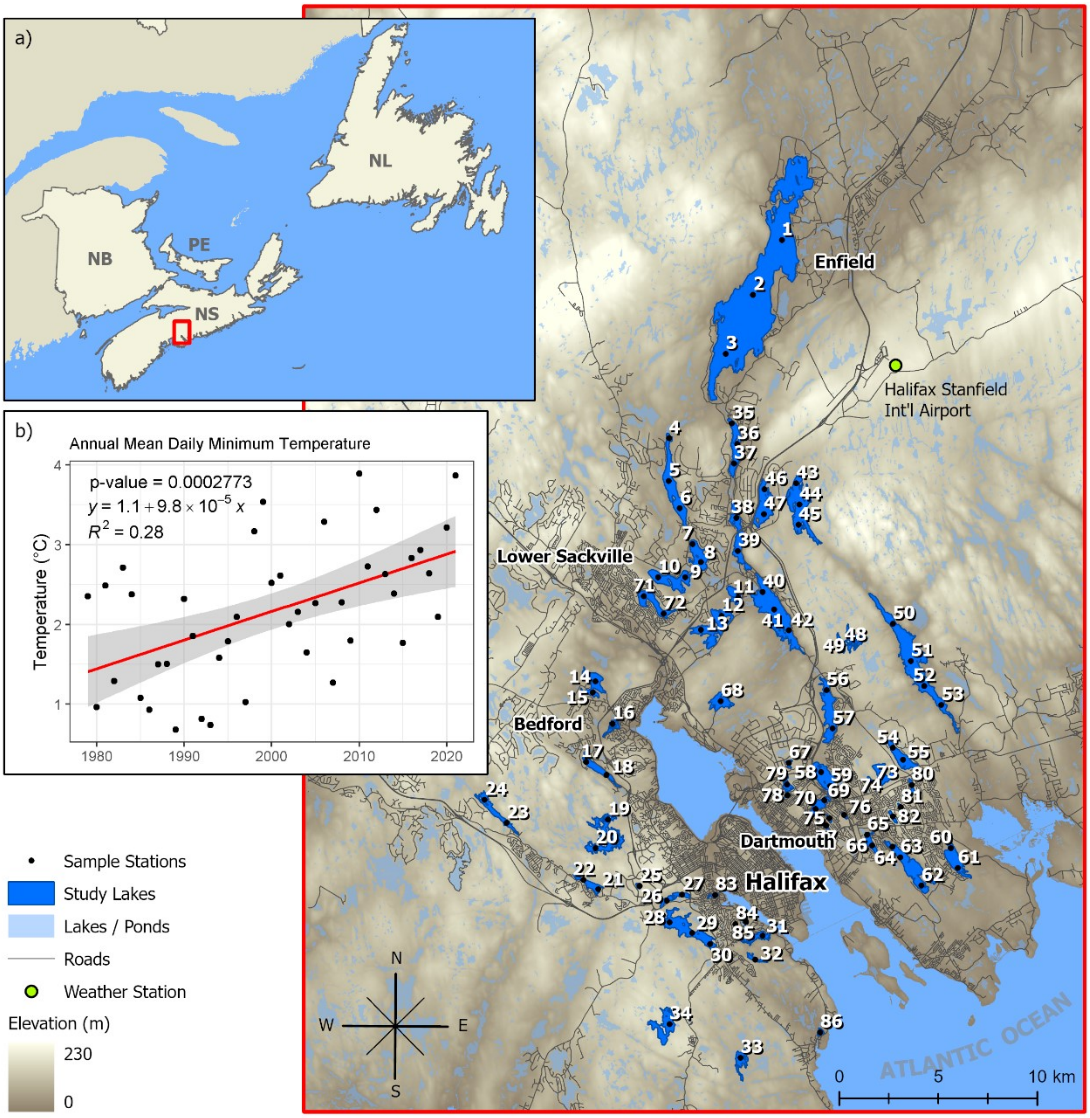

Figure 1.1. *Map depicting study lakes (dark blue) and other water features (light blue), elevation, sample locations (numbered black points correspond to Table A.1, road network (grey lines), and Halifax Stanfield International Airport Weather Station (green point). Inset a): study area situated in Atlantic Canada. Inset b): Annual mean daily-minimum temperatures from 1979 to 2021 (from Halifax Stanfield International Airport Weather Station) plotted along with a linear regression line (red), and the 95% confidence level interval (grey). Map projection: NAD 1983 UTM Zone 20N. Map data sources listed in Table A.4 (Figure from Doucet et al. In Review).*

At the time of the 2000 survey, a doubling in conductivity was observed in almost all of the lakes (Clement et al. 2007). As of 2011, significant increases were also observed in sodium, calcium, magnesium, potassium, chloride, alkalinity, and nitrate (Clement and

Gordon 2019). Notably, these changes were more pronounced in lakes with developed watersheds (Clement et al. 2007; Clement and Gordon 2019).

1.3 Thesis overview and objectives

Emerging water quality concerns in diverse urban lakes were analyzed in this thesis while evaluating widely used and novel monitoring methods. This research largely builds upon the dataset compiled through the SWQS of select HRM lakes, initiated in 1980, which serves as a case study of temperate urban lakes and explores urban development as a possible driver of deterioration, within the context of regional climatic changes and decreases in atmospheric acid deposition. The utility of decadal spring synoptic sampling is explored as is the relevance of trophic state models developed by the OECD in a subset of lakes that were previously understudied (i.e., diverse urban lakes), especially in the context of climate change. The data presented within this thesis serves as a baseline and guide to inform future HRM lake management practices, while also having broader implications for temperate urban lakes in general.

Broadly, this body of research was driven by the following objectives:

1. Identify water quality concerns as of 2021 and trends since 1980 in diverse urban lakes.
2. Investigate urban development as a possible driver of observed changes in water quality (within the context of regional changes in climate and decreases in acid deposition).
3. Evaluate the efficacy of common and novel lake water quality monitoring methods.

Chapter 2 is formatted as a journal article and summarizes the findings of the SWQS that has been performed on a decadal basis since 1980 on ~50 lakes within the HRM while exploring urban development as a possible driver of water quality changes. Chapter 2 addresses the following research questions:

1. How has water quality changed in HRM lakes since 1980?
2. Is urban development driving changes in water quality?

3. How effective is decadal spring synoptic monitoring in detecting changes in lake water quality?

Chapter 3 presents the findings of a supplementary study where trophic state parameters in a subset of the SWQS lakes were tracked over the 2021 open-water season to examine nutrient and productivity dynamics and evaluate the utility of existing models and indicators that are widely used to characterize lake trophic state. The research questions addressed in Chapter 3 are listed below:

1. What level of sampling/monitoring is required to adequately characterize the temporal and spatial dynamics of TP concentrations in diverse urban lakes? And does water chemistry appear to influence these dynamics?
2. Are existing trophic state relationships applicable in lakes that have been altered by both local (urbanization) and regional (climate, acid deposition) environmental changes?

Conclusions drawn from Chapters 2 and 3 are reiterated and synthesized in Chapter 4 and recommendations are made for future research.

CHAPTER 2 – SYNOPTIC SNAPSHOTS: MONITORING LAKE WATER QUALITY OVER FOUR DECADES IN AN URBANIZING REGION

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2.1 Abstract

Synoptic water quality surveys—measuring major ions, nutrients, pH, organic matter, and trace elements—have been conducted in ~50 lakes in the Halifax Regional Municipality, Nova Scotia, Canada, once per decade since 1980. In this study, lake water quality over 40 years was examined and urban development was evaluated as a possible driver of observed changes. Over half of the lakes experienced strong (> 50%) increases in conductivity, iron, sodium, chloride, calcium, and total phosphorus (TP), and strong decreases in acidity (i.e., [H^+]). Between 20% and 50% of the lakes experienced strong increases in nitrate, alkalinity, zinc, color, aluminum, dissolved organic carbon, and magnesium, and strong decreases in manganese and sulphate. In 2021, national guidelines for the protection of aquatic life were exceeded by chloride, aluminum, manganese, and arsenic in certain lakes. Land cover classification from ~1980 and 2020 revealed an increase in urban development in 90% of lake watersheds, which ranged from < 1% to nearly 75% developed in 2020. Urban development was associated with increased chloride, conductivity, sodium, calcium, and TP concentrations. Other parameters appear to be more influenced by hydrology, watershed characteristics, climate, and decreased acid deposition. Results highlight emerging water quality concerns, such as elevated aluminum concentrations, and increased concentrations of chloride, nutrients, and arsenic, that should be the focus of strategic monitoring and mitigation efforts.

Key words: acid deposition, contaminants, land-use change, lake management, remote sensing, synoptic sampling, urban development, water quality

2.2 Introduction

Surface waters are vulnerable to degradation by human activities, including the introduction of contaminants and impacts resulting from urban development, agriculture, and resource extraction (Howell et al. 2012; Ren et al. 2014). Vegetation removal and increased impervious surface coverage affect surface water runoff, increasing delivery of contaminants of both natural and anthropogenic origin to freshwater systems (Hall et al. 1999). Contaminants also reach surface waters through atmospheric transport of industrial emissions, and directly, in the form of wastewater effluent and stormwater inputs. Increases in major ions, nutrients, trace elements, and pH are often detected in waterbodies near urban areas (Howell et al. 2012; Ren et al. 2014; Dugan et al. 2017; Scott et al. 2019). Changes in water chemistry affect the functioning of aquatic systems, including their productivity, community structure, and biodiversity, and may also disrupt physical processes such as thermal stratification and mixing regimes (Novotny and Stefan 2012; Dugan et al. 2017).

On a regional scale, shifts in water quality may also occur due to climate change. Rising temperatures coupled with extreme precipitation events cause increases in nutrient loading, warmer surface water temperatures, increased thermal stratification, and increased acidity (Moore et al. 2008; Paerl et al. 2011; Chapra et al. 2017). In many lakes, warmer air temperatures primarily affect ice cover duration and mixing regimes, increasing the strength and duration of thermal stratification (Paerl et al. 2011; Woolway et al. 2020). This, in turn, may increase internal loading from sediments, such as with phosphorus and arsenic, by creating anoxic conditions in the hypolimnion (Novotny and Stefan 2012; Clark et al. 2021). Climate change also elevates eutrophication risk, and in particular, the risk of harmful cyanobacteria blooms (Moore et al. 2008; Paerl et al. 2011; Pick 2016).

Lake water chemistry is also influenced by morphology, hydrology, and watershed characteristics. Annual flushing rate influences both contaminant loading and residence times (Gorham et al. 1986; George and Hurley 2003; Jones et al. 2008). Vegetation, soil composition, bedrock geology, and the proportion and types of wetlands present also affect key water quality parameters (Gorham et al. 1986; Gergel et al. 1999; McDonald et al. 2004; Clair et al. 2011).

The Halifax Regional Municipality (HRM) is the largest municipality in Atlantic Canada, at nearly 5,500 km^2 in size with a population of ~440,000, up 9% from 2016 (Statistics Canada 2022), making it among the fastest growing cities in Canada (Statistics Canada 2021). Over 1,000 lakes are located within HRM, underscoring the importance of lake management as urban development intensifies. Silt, road salt, nutrients, acid precipitation, and fecal contamination have been identified as major threats to HRM lakes (Stea et al. 2015; Ginn et al. 2015; Clement and Gordon 2019). Other stressors include invasive species, such as the yellow floating heart (*Nymphoides peltata*) proliferating in Little Albro Lake (Darbyshire and Francis 2008), and elevated arsenic levels as a result of historical gold-mining practices and post-mining urbanization, particularly in Lake Charles (Clark et al. 2021).

The Synoptic Water Quality Study (SWQS) of select HRM lakes was initiated in 1980 by federal, provincial, and academic partners to monitor lake health over time by measuring standard water quality parameters (Clement and Gordon 2019). The synoptic surveys occurred on a decadal basis (i.e., 1980, 1991, 2000, 2011, 2021) and included ~50 lakes (50 in 1980; 51 in subsequent years). This study synthesizes the data collected over the 40-year period to identify shifts in water quality and causal factors. The following research questions were addressed:

1. How has water quality changed in HRM lakes since 1980?
2. Is urban development driving changes in water quality?
3. How effective is decadal spring synoptic monitoring in detecting changes in lake water quality?

Based on observations from 1980 to 2011, significant changes in water quality over the 40-year period were anticipated, as was a relationship with urban development (Gordon et al. 1981; Keizer et al. 1993; Clement et al. 2007; Clement and Gordon 2019). Moving forward, the results of this study will inform future lake management efforts by revealing drivers of water quality change and where improvements can be made with regard to land-use management.

2.3 Study site

The first synoptic water quality survey was conducted in the spring of 1980 and included 50 HRM lakes (Table A.1). In 1991, two additional lakes were added to the survey, and another was accidentally omitted, resulting in the set of 51 lakes that were all sampled in 2000, 2011, and 2021 (Table A.1; Fig. 2.1).

The lakes capture a gradient in size, watershed characteristics, location, and exposure to urban development in HRM (Fig. 2.1; Table A.1). Lake surface areas range from 0.02 km^2 to 18.82 km^2, maximum depths from 1.5 m to 65 m, estimated volumes from 47,000 m^3 to 303,068,120 m^3, and watershed areas from ~0.2 km^2 to 369 km^2.

Based on the 1981 – 2010 Climate Normals calculated from the Halifax Stanfield International Airport weather station (Fig. 2.1), daily minimum air temperatures range from -8.8°C in the winter to 12.4°C in the summer. Daily maximums range from -0.1°C to 22.6°C. Air temperatures in HRM have increased over the 40-year study period by ~1°C ($R^2 = 0.28$, $p < 0.001$), based on linear regression of the mean annual minimum daily temperatures from 1979 to 2021 (Fig. 2.1). Minimum- rather than mean-daily temperature was examined due to the strong connection to lake ice coverage (Filazzola et al. 2020). Annual precipitation in HRM totals ~1400 mm with the greatest precipitation during autumn and winter. Precipitation has not significantly increased since ~1980, based on linear regression ($R^2 = 0.02$, $p = 0.34$) (Fig. A.1), but is expected to increase by ~7% over the next 60 years (NSECCU 2014). Temperatures in the region are expected to increase by > 2°C in the next 60 years (NSECCU 2014).

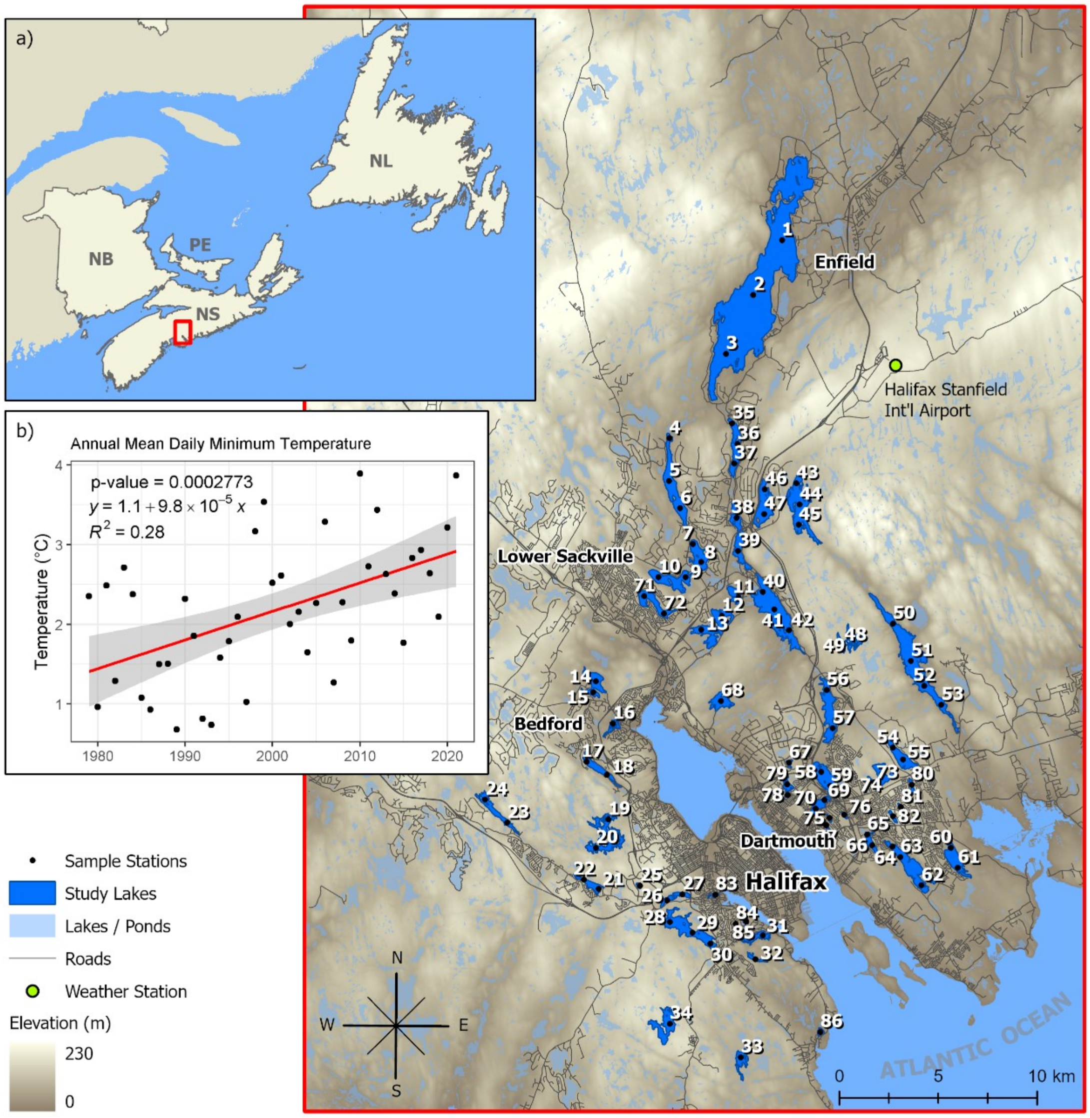

Figure 2.1. *Map depicting study lakes (dark blue) and other water features (light blue), elevation, sample locations (numbered black points correspond to Table A.1, road network (grey lines), and Halifax Stanfield International Airport Weather Station (green point). Inset a): study area situated in Atlantic Canada. Inset b): Annual mean daily-minimum temperatures from 1979 to 2021 (from Halifax Stanfield International Airport Weather Station) plotted along with a linear regression line (red), and the 95% confidence level interval (grey). Map projection: NAD 1983 UTM Zone 20N. Map data sources listed in Table A.4.*

Five wastewater treatment facilities (WWTF) discharge into surface waters in the study area, with all but one utilizing tertiary treatment (Table A.2). Three lakes directly receive WWTF effluent, including William, Fletcher, and Grand, while another four lakes are indirectly affected, including Kinsac, Soldier, Miller, and Thomas (Table A.2). Residences located beyond the boundary of the municipal sewer system rely on septic systems to treat wastewater. A minimum of 40,000 septic systems are located in HRM (Halifax Regional Council 2007), accounting for ~14% of the municipality's population (Statistics Canada 2011; Statistics Canada 2015).

2.4 Materials and methods

2.4.1 Synoptic Water Quality Study design

The synoptic sampling approach, where numerous water quality measures are collected over a brief period of time, captures water quality conditions among lakes at a single point in time. This time-sensitive sampling design was enabled by collecting most samples by helicopter and using boats where lakes were not accessible by helicopter. Typically, the collection took place within a single day, thus reducing temporal variability among lakes (Clement and Gordon 2019). Variability in water chemistry within each lake was reduced by collecting surface samples in the early spring, immediately following ice-out, when lakes were mixing. Additionally, multiple surface samples were collected and compared for large lakes, and lakes having distinct basins (50% of lakes). Quality control measures included replicate sampling in a subset of lakes and verifying agreement among replicates, as well as the collection of field blanks to assess procedural variability.

Following collection, surface water samples were transported to a lab and divided, and the subsamples were either analyzed onsite or were delivered to commercial, government, and academic laboratories for immediate analysis. Each sample was measured for a standard set of water quality parameters, a subset of which were selected for analysis in this study (Table A.3). Analytical methods were kept as consistent as possible over the years but several have changed since 1980. To account for this, alkalinity measurements were "binned" into categorical descriptors to facilitate comparisons among years, while reactive silica and ammonia were excluded from among-year comparisons and trend analyses altogether. Certain trace element measurements in 1991 were sporadic and inexplicably high and were likely a result of contamination or analytical problems (Clement and Gordon 2019). Similarly, dissolved organic carbon (DOC) measurements from 1991 may have been underestimated by as much as 20-40% due to the use of the wet oxidation method (Koprivnjak et al. 1995). As a result, 1991 measurements of trace elements and DOC were excluded from all subsequent analyses. All analytical errors, major differences, questionable measurements, and discarded values have been noted in Tables A.1 and A.3. Detailed accounts of sample collection, processing, quality control measures, and analysis for 1980, 1991, 2000, and 2011 can be found in the former reports associated with the Synoptic Water Quality Study of Selected Halifax-area Lakes (Gordon et al. 1981; Keizer et al. 1993; Clement et al. 2007; Clement and Gordon 2019).

2.4.2 Spatial analysis

2.4.2.1 Watershed delineation

The watershed of each study lake was delineated using the Arc Hydro workflow and toolset in ArcGIS Pro 2.7.3. This workflow uses a digital elevation model (DEM), a stream network, and the lake's approximate discharge location to model the natural flow of water over the landscape and identify the boundary of the watershed (Table A.4). A 20-m resolution DEM was used to delineate most watersheds, however, where a higher resolution was needed (i.e., for certain small watersheds) a 5-m resolution DEM was used. Manual adjustments were required for many watersheds to account for the municipal stormwater system and other infrastructure (e.g., roads) that interrupt the natural flow of water across the landscape.

2.4.2.2 Satellite imagery classification

To evaluate the impact of land-use change on water quality parameters, past and present satellite imagery encompassing the HRM was obtained and classified. The study area falls within a single Landsat scene (located at Path 008, Row 029) and the images were selected from the summer months (July to September) to ensure that vegetation was distinguishable from other landcover types. Two Landsat images (30-m spatial resolution) were obtained from the United States Geological Survey (USGS) Earth Explorer, one from the early 1980s (Landsat 4 TM, Collection date: Sept 14, 1982) and the second from 2020 (Landsat 8 OLI, Collection date: July 28, 2020). Although cloud cover and cloud shadow accounted for < 3% of the approximate study area in the 1982 image, enough of the land features were obscured that a 1985 image (Landsat 5 TM, Collection date: Sept 30, 1985) was also obtained and classified. Map algebra was then used to mosaic the classified outputs of both images such that pixels recognized as cloud and cloud shadow in the 1982 output were replaced with pixels from the 1985 output.

Unsupervised (Iterative Self-Organizing Data Analysis Techniques, ISODATA) classifications were performed on false color composites using visible red, near-infrared, and short-wave infrared bands as input channels. This spectral band combination highlights vegetated areas and is also useful for identifying water features. All classifications were performed in ArcGIS Pro 2.7.3 using the ISO Cluster classifier (iterations: 40, clusters: 20). Resulting spectral classes were aggregated to three informational classes: water, developed, and undeveloped. A fourth class for cloud and cloud shadow was included for the 1982 image. Wetlands and barren areas (i.e., areas with exposed bedrock) were frequently misclassified as developed in both the 2020 and mosaicked 1982 outputs. Delineations of these land covers were obtained (sources listed in Table A.4), rasterized, and used to amend the classified outputs through map algebra. Although the delineations do not date back to 1980, it was assumed that these land areas remained consistent.

Following the manual amendments, accuracy assessments were performed on both outputs by generating a random sample of 500 points (stratified to class percentages) and assigning each to their appropriate informational class. To assist with this process, different composites were used to highlight certain features in the reference image and ancillary data was used when available and needed. Both outputs achieved a Kappa statistic > 0.85 and overall accuracies > 95% (Table A.5). Detailed accuracy results, including user's and producer's accuracies for each informational class can be found in Table A.5.

Land covers were then quantified from the thematic outputs of the satellite imagery classification by calculating the proportion of pixels of each land cover within each watershed, including water surfaces.

2.4.3 Data analysis

2.4.3.1 Data preparation

For all statistical analyses, $p < 0.05$ was accepted for statistical significance. Lake morphometric data, including volume, surface area, and maximum depth, were obtained from various sources. All statistical analyses were performed in R (Version 4.1.2). Twenty-three water quality parameters from the synoptic datasets were analyzed (Table A.3). pH measurements were converted to $[H^+]$ for all analyses, apart from the ordinations. Each synoptic dataset was screened for outliers and errors. Extreme outliers were either flagged or removed altogether (Table A.3). Missing data was addressed differently for each of the analyses, and parameters or lakes with missing data were only omitted when necessary. When multiple samples were collected from a lake, the mean value for each parameter was calculated and used for all analyses. Where values were below the detection limits, half the detection limit was used for all analyses.

Changes in water quality were calculated by subtracting values measured at the earliest time point (typically 1980, but 1991 or 2000 for certain lakes and parameters) from those measured in 2021. Likewise, changes in the proportion of urban development within lake watersheds were calculated as the difference between the proportion developed in 2020 and the proportion developed in ~1980.

2.4.3.2 Principal component analysis of 2021 measurements

Principal component analysis (PCA) was performed on twenty-three water quality parameters from the 2021 survey (Table A.3) to summarize variation and explore gradients. Data were scaled and centered (to zero) to account for differences in units. PCA biplots were generated to enable the examination of lakes in ordination space, with lakes color-coded by the proportion of urban development within their watersheds in 2020.

2.4.3.3 Trend analyses

To examine region-wide differences in water quality among years, the non-parametric Kruskal-Wallis test was used. Pairwise comparisons were made using the non-parametric post hoc Dunn's test (Bonferroni adjusted), and boxplots were constructed for each parameter (Fig. A.2a-v). Differences in alkalinity among years was examined by comparing the proportion of lakes falling into each "bin" at each point in time. To examine trends within the lakes individually, percent change of each parameter in each lake was calculated and changes > 50% were presented in a heat map. Additionally, a second heat map was generated containing the z-score for each measurement for each lake in 2021 to enable the visual examination of each measurement relative to all study lakes and thus give context to the observed percent change.

Linear regression (1,122 separate analyses in total) was performed for each parameter for each lake utilizing the available data points (typically n = 5 but limited to n = 4 and n = 3 for certain lakes and parameters). A subset of the corresponding line plots is presented, while the remainder can be found in the Supplement (Fig. A.3a-u).

2.4.3.4 Multiple linear regression

Multiple linear regression analyses were used to explore relationships between the observed changes in water quality and possible explanatory variables, such as urban development and watershed characteristics. Several explanatory variables were compiled and summarized in Table 2.1, which presents the abbreviated parameter names that will be used in the paper. Changes in each parameter comprised the response variables in the analyses, denoted as "ΔParameter name" (e.g., ΔChloride).

Table 2.1. *Abbreviations and descriptions for explanatory variables used in multiple regression analyses. *Not available for Parr (Governors) Lake or Whimsical Lake.*

Abbreviation	**Description**
dev_1980	Proportion of watershed developed in ~1980
dev_2020	Proportion of watershed occupied by development in 2020
dev_change	Change in proportion of watershed developed from ~1980 to 2020
road_density	Road density within watershed (km/km^2)
flush_proxy	Total watershed area / lake surface area (flushing rate proxy)
wetland	Proportion of watershed occupied by wetlands
surface_area	Lake surface area (km^2)
watershed	Watershed area (km^2)
volume*	Estimated lake volume (m^3)
max_depth*	Lake maximum depth (m)

Linear regression was used to assess the linearity of the relationships between the twenty-three response variables and each explanatory variable prior to including the explanatory variables in the multiple regression analyses. Multicollinearity among the explanatory variables was examined through pair plots (Fig. A.4) and variables, including “dev_2020” and “road_density,” were removed from the analysis as they were identified as being highly collinear with “dev_1980”. As such, any significant relationships between “dev_1980” and the response variables can be assumed to apply to “dev_2020” and “road_density” as well (Fig. A.4). Stepwise model selection (backward and forward) was used to identify the best model (i.e., having the lowest Akaike information criterion (AIC) value) for each response variable. The models were then tested for violations of the assumptions of multiple linear regression, including independence, linearity, residual homoscedasticity, and residual normality (Table A.6).

2.4.3.5 Climate data collection and analysis

Due to the influence of precipitation and air temperature on lake water quality in the short term, hourly data from the 12- and 6-month periods prior to each sampling event were obtained and mean minimum daily temperature and total precipitation were calculated for each interval. This aimed to determine if differences in water quality parameters among years could, in part, be explained by weather patterns in the months leading up to each survey.

2.5 Results and discussion

2.5.1 Lake and watershed characteristics

HRM lakes ranged from clear to highly colored, with some of the lowest color measurements recorded from Chocolate, First Chain and Second Chain, Micmac, and Banook, while Governors (Parr), Power Pond, Long Lake, and Colpitt were among the most colored. Color increased in 65% of the lakes, with color more than doubling in five of the most colored lakes (Fig. A.3g). pH ranged from 4.4 to 7.6 in 2021, with nearly 40% of the lakes falling below the guideline identified by the Canadian Council of Ministers of the Environment (CCME), which recognizes that toxicity for aquatic life increases below pH of 6.5 (CCME 2003). The lowest pH were detected in undisturbed watersheds and those influenced by acid rock drainage, including First Chain Lake and

Second Chain Lake (Tarr and White 2016). Based on 2021 spring total phosphorus (TP) concentrations, the study lakes ranged from ultra-oligotrophic (< 4 μg/L) to meso-eutrophic (20 – 35 μg/L), with three lakes, Chocolate, Topsail, and Major, falling into the former category, and two lakes, Bissett and Settle, falling into the latter (CCME 2004). The majority of the lakes were either oligotrophic (~60%) or mesotrophic (~30%), having TP concentrations of 4-10 μg/L and 10-20 μg/L, respectively (CCME 2004).

Paved road densities within the watersheds, based on current provincial road network data (Table A.4), reveal a mean density of 4.13 ± 3.00 km/km^2, with no paved roads in the watersheds of either Bell or Spruce Hill Lake. The greatest density of roads was found in Oathill Lake's watershed at 11.62 km/km^2. Overall, urban development in 2020 ranged from < 1% in Spruce Hill Lake's watershed to nearly 75% in Oathill Lake's watershed (Fig. 2.2). Ninety percent of the lakes experienced an increase in urban development within their watersheds over the ~40-year period, nearly half of which increased by > 10% points (Fig. 2.2). Bayers Lake had the greatest increase in urban development, having an additional 48% of its watershed developed in 2020 compared to ~1980 (Fig. 2.2).

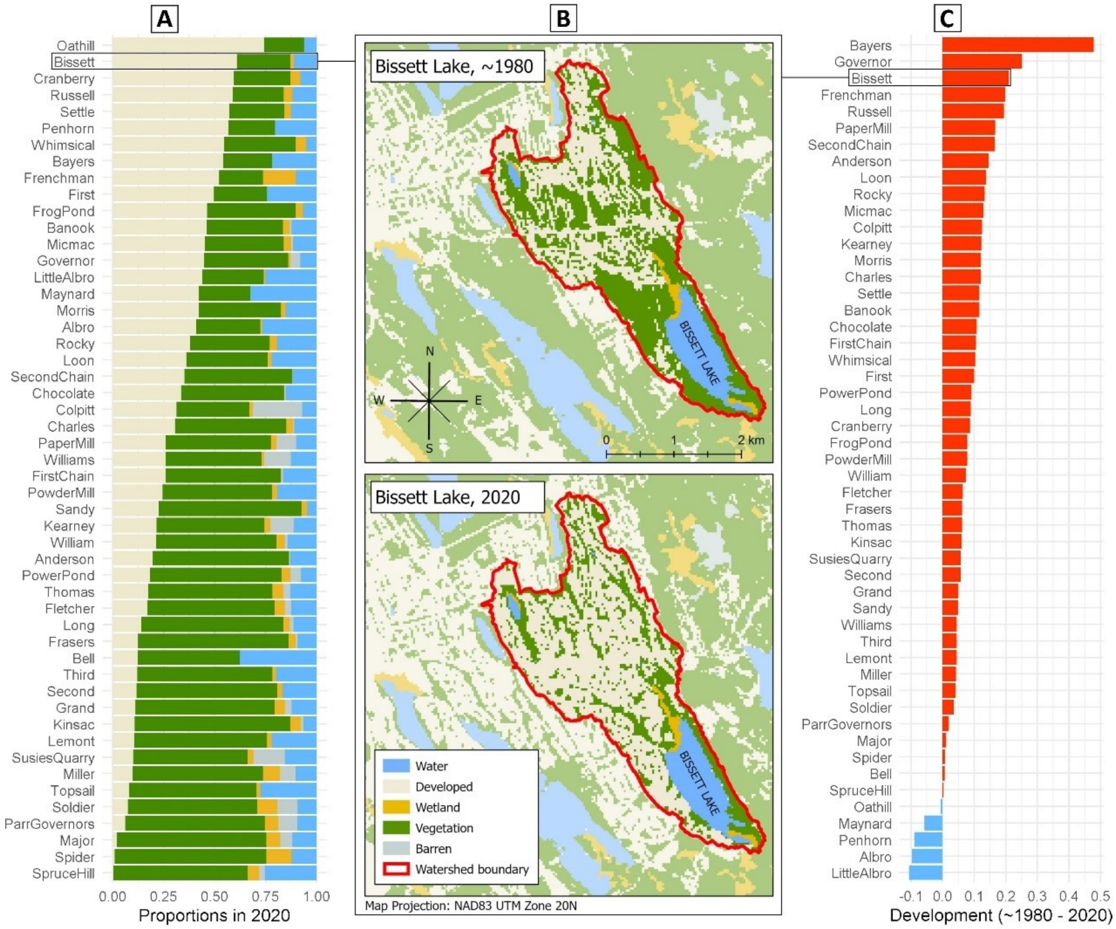

Figure 2.2. *A) Land cover proportions within each watershed in 2020, colors correspond to panel B. B) Bissett Lake's watershed and land cover types identified through the unsupervised classification of satellite imagery from ~1980 (top) and 2020 (bottom). C) Change in urban development within each watershed from ~1980 to 2020 expressed as a proportion.*

Generally, the study lakes remained within the CCME guidelines for the protection of aquatic life; however, there are a few notable exceptions, including concentrations of chloride in 20% of the lakes, arsenic in one lake, aluminum in 29% of the lakes, and manganese in two lakes. It is also worth noting that certain guidelines do not adequately protect freshwater ecosystems, such as for chloride concentrations, suggesting that the number of study lakes at risk of ecological harm is likely higher than reported here (Hintz et al. 2022).

As of 2021, chloride ion concentrations in nearly 20% of the study lakes exceeded the recommended long-term exposure limit (120 mg/L) for the protection of aquatic life in

Canada (CCME 2011). The highest concentration was observed in Frenchman Lake at 408 mg/L, exceeding concentrations in the other study lakes by a wide margin but remaining below the short-term exposure guideline of 640 mg/L (CCME 2011). In contrast, only one lake (Frog Pond at 125 mg/L) exceeded the guideline in 1980. Chloride concentrations in lakes have been found to peak in the spring, and as such, the measurements reported here likely represent annual maximum concentrations (Scott et al. 2019). The application of road de-icing salts has been identified as a major cause of increasing chloride concentrations in surface waters, a trend that has been observed across Canada's urban regions, where toxicity thresholds are often exceeded (Novotny and Stefan 2012; Kilgour et al. 2013; Dugan et al. 2017; Scott et al. 2019). Over 5 million tonnes of salt are applied to Canadian roads each winter, with the greatest amount per unit area being applied in Nova Scotia (Morin and Perchanok 2000; Environment Canada 2012). Elevated chloride concentrations affect the functioning of freshwater systems, including their productivity, community structure, and biodiversity (Dugan et al. 2017). Further, increased salinity has been found to cause stratification in dimictic lakes that inhibits natural mixing regimes, exacerbating eutrophication by further depleting dissolved oxygen levels near the water-sediment interface and facilitating the release of sediment phosphorus (Novotny and Stefan 2012), and likely other contaminants.

Arsenic concentrations in Lake Charles, which is adjacent to the historical Montague Gold District, already exceeded the CCME guideline of 5 µg/L when the parameter was first reliably measured in 2000, and that value has more than doubled in the 20 years that followed (CCME 2001). Increases have been attributed to the legacy effects of historical gold mining practices. A recent study of sediment cores from Lake Charles revealed that the highest arsenic concentrations exist at the water-sediment interface, despite mining activities ceasing ~80 years prior (Clark et al. 2021). The continued release of arsenic is expected if conditions at the water-sediment interface (e.g., anoxic conditions) favor its release (Hull et al. 2021; Clark et al. 2021). Arsenic can bioaccumulate in organisms, and a loss of invertebrate diversity within Lake Charles was observed (LeBlanc et al. 2020; Clark et al. 2021). Additionally, arsenic concentrations in both Lake William and Lake Micmac (which receive drainage from Lake Charles) have increased by 81% and 35% since 2000, respectively. Elevated arsenic concentrations are also observed in groundwater in the area due to the geology of the region and specifically the presence of arsenic sulfide within the gold-bearing Goldenville Formation (AECOM 2013). This may in part explain the increases observed in nearby Third Lake, where arsenic concentrations were ten times higher than in 2000, resulting in the second highest concentration in 2021 at 3.1 µg/L. Arsenic levels also increased nearly eight-fold in Kinsac Lake, which is located roughly 10 km from Lake Charles (Fig. 2.1). Elevated arsenic levels are not unique to this region and have been observed across the province including in drinking water supplies, although uncertainty exists regarding the extent to which arsenic, which is a known carcinogen, may be affecting human health in Nova Scotia (Saint-Jacques et al. 2018).

Aluminum, iron, and manganese are the most abundant trace elements within the lakes, with high concentrations of zinc and copper also being observed (Clement and Gordon 2019). Of these elements, iron and zinc concentrations remained below CCME guidelines when site specific toxicity modifying factors (i.e., hardness, pH, and DOC) were applied on a lake-by-lake basis (CCME 2018; ECCC 2019). Conversely, nearly 30% of the study lakes exceeded aluminum toxicity thresholds in 2021(ECCC 2021a). As with the other trace elements, the highest concentrations were observed in lakes impacted by acid rock drainage, caused by the oxidation and weathering of the pyrite-containing Halifax Formation (Gorham et al. 1986; Fox et al. 1997; Tarr and White 2016). First Chain and Second Chain Lakes had the highest aluminum concentrations at 1.9 mg/L and 3.0 mg/L, respectively. The effects of elevated aluminum concentrations on various fish species are well documented (ECCC 2021a) and coupled with recent reports of rising aluminum concentrations in Nova Scotia lakes and rivers, underscores the need for future studies (Sterling et al. 2020; Redden et al. 2021).

In contrast, only Bayers Lake and First Chain Lake exceeded manganese toxicity thresholds, (which vary based on hardness and pH) having concentrations of 324 µg/L and 284 µg/L, respectively in 2021 (CCME 2019). It is unclear whether copper toxicity thresholds were exceeded as copper's toxicity is dependent upon eleven different water quality parameters, making it difficult to reliably estimate a threshold for each lake individually (BC MECCS 2019). However, comparing 2021 copper concentrations to the range and quantiles of copper concentrations in Nova Scotia surface waters reported by Environment and Climate Change Canada revealed that < 10% of the lakes fell below the provincial median concentration, while > 70% fell within the 75th percentile, and nearly 30% were within the 90th percentile, including Bayers Lake and Second Chain Lake (ECCC 2021b). Additionally, despite the relatively low levels of development within the watersheds of Grand and Major Lakes (11% and 2% in 2020, respectively), both were among those lakes with copper concentrations in the 90th percentile (ECCC 2021b). Both manganese and copper are biologically essential elements that become toxic to aquatic life at elevated concentrations (US EPA 2007; CCME 2019). Sources of the elements include the natural weathering and erosion of geological deposits and soils, as well as anthropogenic disturbances such as development and resource extraction activities (BC MECCS 2019; CCME 2019).

Three components were identified by the PCA that together account for 67% of the variance (Fig. A.5). Broadly, PC1 appears to be driven by major ion concentrations, PC2 by trace elements, and PC3 by nutrients (Table A.7). Color-coding the lakes based on their level of urban development in 2020 reveals that only PC1, and thus major ion concentrations, separate out the watershed development groups (Fig. 2.3). Lakes located in less developed watersheds (< 20% developed) generally appear to be more colored and among the most acidic, with high DOC concentrations, and low concentrations of major ions and trace elements (Fig. 2.3). Few lakes score high on PC2; however, those having less than 20% development within their watersheds have consistently low PC2 scores (Fig. 2.3). This suggests that while some degree of connection exists between level of development and trace element concentration, other factors are important. As expected, Chocolate Lake, First Chain Lake, Second Chain Lake, and Bayers Lake load most on PC2, corresponding to their high trace element and sulphate concentrations (Fig. 2.3). All four lakes are in moderately to highly developed watersheds (> 20% developed), yet are also among the most acidic, unlike other developed lakes (Fig. 2.3). This can be attributed to the acid rock drainage occurring within their watersheds, which also contributes to their high trace element concentrations (Gorham et al. 1986; Tarr and White 2016).

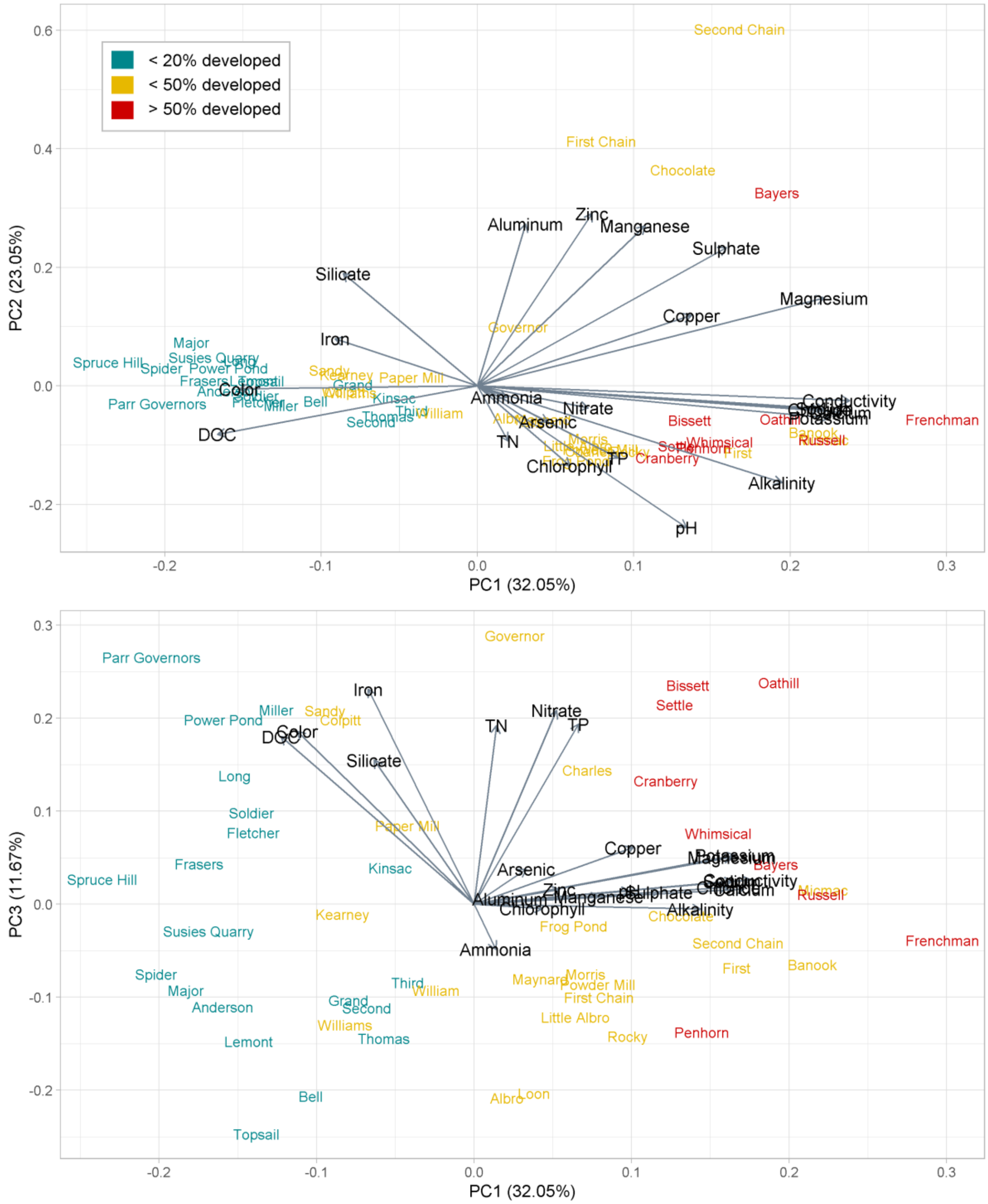

Figure 2.3. *PCA biplots of 2021 data with lakes color-coded by proportion of watershed developed in 2020.*

A range of scores on PC3 can be observed for lakes of all three levels of urban development (Fig. 2.3). Notably, Oathill, Bissett, and Settle Lake appear to have among the highest nutrient concentrations and are also among the most developed (Fig. 2.3).

However, a number of lakes having moderately developed watersheds (e.g., Governor and Charles) and mostly undeveloped watersheds (e.g., Miller and Parr (Governors)) also load on PC3 (Fig. 2.3).

This could, in part, be due to the high variability of nutrients, but also indicates that other factors may be driving nutrient concentrations. Lakes occurring along the urban-rural fringe tend to be at a higher risk of eutrophication due to the use of septic systems (Moore et al. 2003). Conventional septic systems use a settling tank and drainage field to filter and disinfect the wastewater but remain a significant non-point source of nutrients to surrounding waterbodies, and their influence on eutrophication risk may even exceed that of WWTF effluent (Moore et al. 2003; McCray et al. 2005). This may, in part, explain why the lakes with the least developed watersheds exhibit such variability in nutrient levels (Fig. 2.3), and further suggests that rural residential expansion and the use of septic systems may be significant contributors to elevated nutrients and thus eutrophication risk (Moore et al. 2003).

2.5.2 Trend analyses

Collective analysis of each parameter on all 51 lakes using Kruskal-Wallis tests revealed significant differences among years for chloride ($\chi^2(4) = 22.9$, $p < 0.001$, n = 240), sodium ($\chi^2(4) = 23.9$, $p < 0.0001$, n = 240), and conductivity ($\chi^2(4) = 37.9$, $p < 0.0001$, n = 245). Concentrations of chloride were significantly higher in 2000, 2011, and 2021, when compared to the concentrations measured in 1980 ($p < 0.05$, $p < 0.0001$, and $p < 0.01$, respectively) (Fig. 2.4). As expected, the differences among years in chloride concentration aligned closely with those of both sodium concentration and conductivity (Fig. A.2p, h).

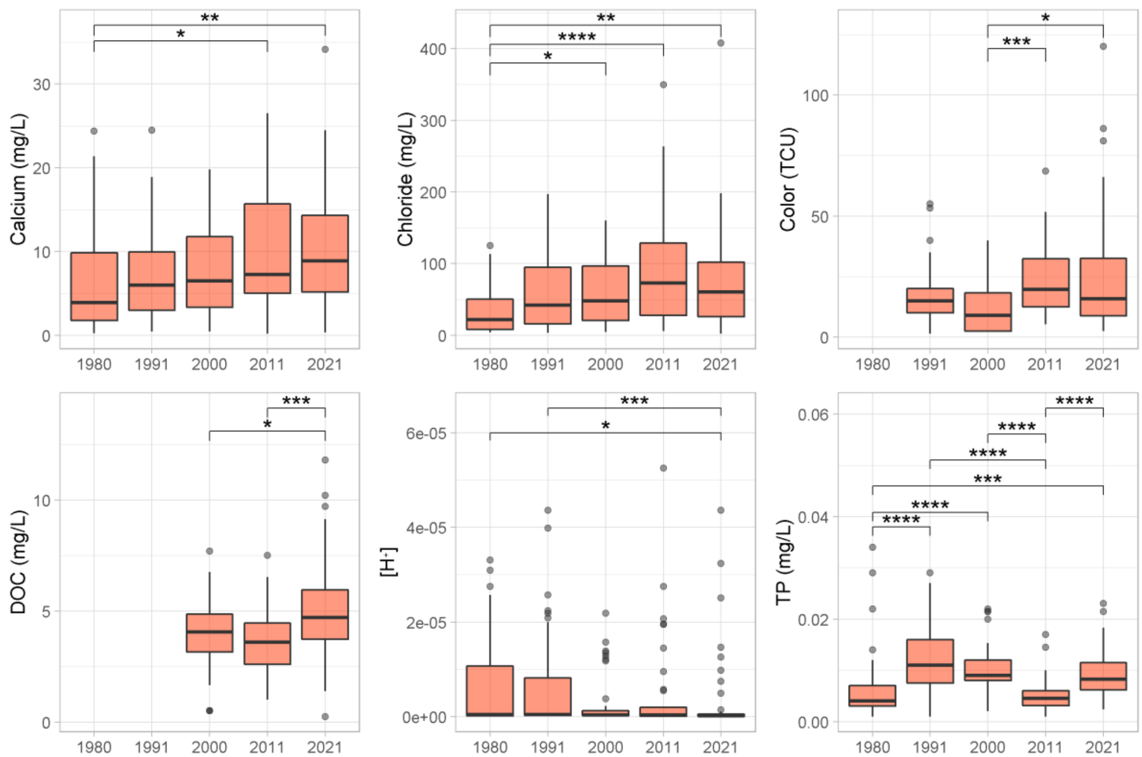

Figure 2.4. *Boxplots for six parameters with significant differences among years indicating significance of pairwise comparisons where p < 0.05 (*), p < 0.01 (**), p < 0.001 (***), and p < 0.0001 (****).*

Although significant differences were observed among years for the three nutrient parameters, nitrate ($\chi^2(4) = 30.0$, $p < 0.0001$, $n = 240$), total nitrogen (TN) ($\chi^2(4) = 19.6$, $p < 0.001$, $n = 240$), and TP ($\chi^2(4) = 67.5$, $p < 0.0001$, $n = 235$), no clear patterns were observed over time or among the three parameters (Fig. 2.4, Fig. A.2q, t, u). This is likely a result of nutrients exhibiting high variability, that could be partially explained by the conditions around the time of each survey among years (i.e., temperature, precipitation, etc.). Importantly, this variability may obscure trends in nutrient concentrations and suggests that spring synoptic sampling on a decadal basis may not be an adequate monitoring approach for nutrient trends. To improve detection of eutrophication, combined monitoring and paleolimnological approaches of HRM lakes could yield important insights of long-term trends (Ginn et al. 2015; Clark et al. 2021).

Collective analysis of calcium found significant differences among years ($\chi^2(4) = 15.7$, $p < 0.01$, $n = 240$), while pairwise comparisons revealed that concentrations in 1980 were significantly lower than those in 2011 ($p < 0.05$) and 2021 ($p < 0.01$), while there were no significant differences among the means of the subsequent four surveys (Fig. 2.4). Although it is possible that calcium increases observed in the last 20 years indicate a recovery from acid deposition, calcium levels have failed to show signs of recovery in many Nova Scotia lakes and rivers as recently as 2019 (Redden et al. 2021), making it more likely that human activities causing the disturbance of bedrock and soil or other anthropogenic sources of calcium (e.g., wastewater effluent, soil amendments, concrete leaching) are responsible for the observed increases (Potasznik and Szymczyk 2015; Kaushal et al. 2017).

Significant differences among years were observed for color ($\chi^2(3) = 18$, $p < 0.001$, $n = 200$), DOC ($\chi^2(2) = 16.69$, $p < 0.001$, $n = 153$), and iron ($\chi^2(2) = 27.29$, $p < 0.0001$, $n = 150$) (Fig. 2.4). Collectively, color measurements in 2011 and 2021 were significantly higher than those in 2000 ($p < 0.001$ and $p < 0.05$, respectively), while both DOC and iron concentrations in 2021 were significantly higher than those measured ten ($p < 0.001$; $p < 0.0001$) and twenty years prior ($p < 0.05$; $p < 0.0001$) (Fig. 2.4, Fig. A.2k). Increases in color can likely be attributed to the concurrent increases in DOC and iron, as both constituents are contributors to lake color. Recent increases in color, DOC, and iron have been observed in other lakes across the province, and have, in part, been attributed to regional decreases in acid deposition following legislation and emissions control (Clair et al. 2011; Redden et al. 2021).

[H^+] was found to differ significantly among years ($\chi^2(4) = 18.3$, $p < 0.01$, $n = 240$), as measurements in 2021 were significantly lower than those measured in 1980 ($p < 0.05$) and 1991 ($p < 0.001$), corresponding to higher pH values in 2021 (Fig. 2.4). Similarly, alkalinity appears to have increased over the 40-year period, with a smaller proportion of study lakes falling under the United States Environmental Protection Agency's (US EPA) categorization of "Endangered to Acidified" (< 5 mg $CaCO_3$/L) and a larger proportion with alkalinity measurements exceeding 20 mg $CaCO_3$/L and thus falling into the "Not Sensitive" category (Table A.8; Fig. A.6) (Godfrey et al. 1996). This may, in part, explain the significantly lower manganese concentrations observed in 2021 compared to 2000 ($\chi^2(2) = 7.12$, $p < 0.05$, $n = 150$), as manganese concentrations, along with that of aluminum, copper and zinc, have been found to decline following the addition $CaCO_3$

(White et al. 1984). These observed increases in pH and alkalinity may in part signal chemical recovery due to decreasing acid deposition in the region, but, as with calcium concentrations, are likely also a result of anthropogenic sources of constituents contributing to alkalinity (Kaushal et al. 2017; Redden et al. 2021).

Over half of the lakes experienced strong increases (> 50%) in conductivity (80% of lakes), iron (71% of lakes), sodium (71% of lakes), chloride (61% of lakes), calcium (59% of lakes), and TP (59% of lakes) (Fig. 2.5A). Strong increases also occurred in nitrate in 49% of the lakes, in color in 47%, alkalinity in 37%, zinc in 31%, aluminum and DOC in 25%, and magnesium in 24% (Fig. 2.5A). Strong decreases (> 50%) occurred in $[H^+]$ (i.e., acidity) in 73% of the lakes, manganese in 35% of the lakes, and sulphate in 22% of the lakes (Fig. 2.5A). Examination of the heat maps suggests that urban development may influence a number of parameters, such as with color, where increases were typically observed in less developed lakes and decreases were observed in those having more developed watersheds (Fig. 2.5A). In contrast, pronounced increases in TP were observed in the most developed lakes, while the few that saw TP decline were located in less developed watersheds (Fig. 2.5A; Fig. A.3t). This underscores the need for focused study and management regarding eutrophication risk in HRM lakes, given expected development pressures in many watersheds.

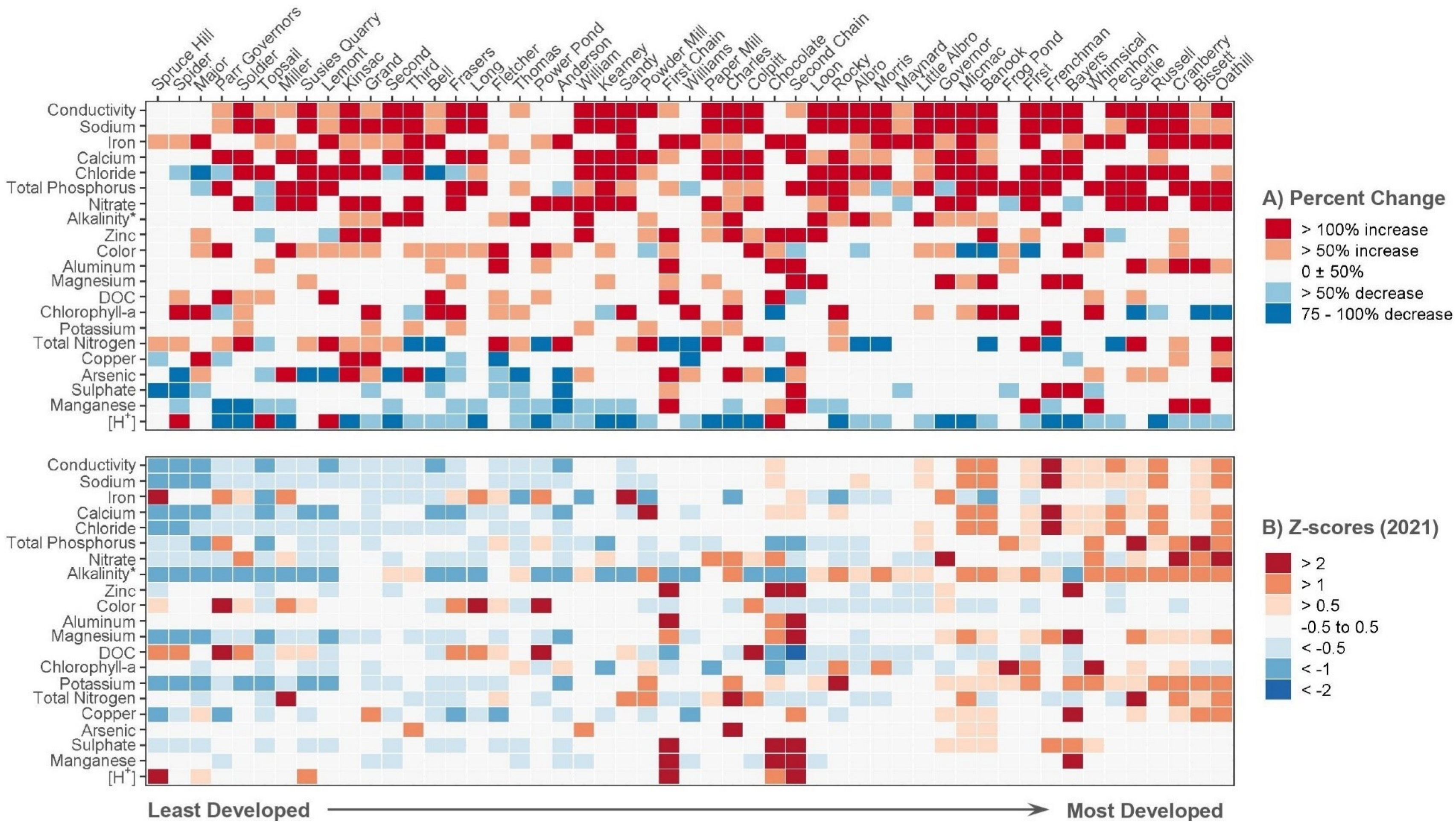

Figure 2.5. *A) Heat map depicting percent change over ~40 years for select parameters in each lake. B) Heat map depicts z-scores (standard scores) calculated for each parameter for each lake, illustrating how each measurement compares to those from the rest of the study lakes. Lakes are ordered from least to most developed. *Binned alkalinity values used.*

Figure 2.5B reveals strong relationships between urban development level and several parameters, including conductivity, sodium, chloride, calcium, alkalinity, magnesium, and potassium, with z-scores > 0.5 in many of the most developed lakes, and < -0.5 in the least developed lakes. This relationship was less pronounced but also apparent for TP, nitrate, and copper (Fig. 2.5B). Despite the relatively constant percent increases across development levels in many of these parameters (i.e., conductivity, sodium, calcium, chloride, TP, and nitrate) (Fig. 2.5A), these z-scores reveal that developed lakes have experienced increases of greater magnitude (Fig. 2.5B). For example, while the conductivity in both Soldier Lake (7% developed) and Oathill Lake (74% developed) increased by > 100% since 1980 (Fig. 2.5A), conductivity in Soldier Lake in 2021 was only 66 μS/cm higher, while conductivity in Oathill Lake increased by 335 μS/cm (Fig. A.3h).

2.5.3 Multiple linear regression

Multiple linear regression analyses were used to explore causal factors of water quality changes, and identified factors contributing to changes in chloride, magnesium, color, DOC, TP, sulphate, and calcium over the duration of the study period (Table 2.2). Due to the high correlation among chloride, sodium, and conductivity, only the model generated for chloride is presented. All models in Table 2.2, apart from the DOC change model, failed the assumption of residual normality, and violations of the independence assumption were detected for several models, including for ΔDOC ($p = 0.047$), ΔSulphate ($p = 0.037$), and ΔCalcium ($p = 0.025$) (Table A.6). Additionally, the study design prevented observations from being truly independent as their geographic locations could be influential. These violations were deemed acceptable as the intention of this analysis was to explore potential causal factors as opposed to producing predictive models.

Table 2.2. *Summary of regression models indicating explanatory variables that may be driving the observed changes in certain water quality parameters (n = 51). *Similar models were obtained for sodium and conductivity, †independence assumption violated.*

Response Variable	Model Adj. R^2	Model Significance	Explanatory Variables	Coefficient Estimate	Coefficient Significance
ΔChloride*	0.31	$p < 0.0001$	dev_1980	+ 190.9	$p < 0.001$
			dev_change	+ 290.9	$p < 0.01$
ΔMagnesium	0.35	$p < 0.001$	dev_change	+ 4.2	$p < 0.001$
ΔColor	0.30	$p < 0.0001$	flush_proxy	+ 0.1	$p < 0.01$
			dev_1980	- 27.1	$p < 0.01$
ΔDOC†	0.19	$p < 0.01$	flush_proxy	+ 0.01	$p < 0.05$
			wetland	+ 12.7	$p < 0.05$
ΔTP	0.17	$p < 0.01$	dev_1980	+ 0.02	$p < 0.01$
ΔSulphate†	0.14	$p < 0.01$	dev_change	+ 42.0	$p < 0.01$
ΔCalcium†	0.12	$p < 0.01$	dev_change	+ 24.2	$p < 0.01$

Changes in chloride over the 40-year period had a positive relationship with both the level of development present in ~1980, as well as the change in development over the study period (Table 2.2). This indicates that lakes that experienced the greatest increases in chloride concentration also tended to have had the highest proportions of urban development in their watersheds.

Development level change was found to account for 35%, 14%, and 12% of the variability in the ΔMagnesium, ΔSulphate, and ΔCalcium concentrations, respectively (Table 2.2). These positive relationships indicate that lakes having experienced the greatest amounts of urban development since ~1980 also recorded the greatest increases in magnesium, sulphate, and calcium concentrations, and the largest decreases in sulphate were observed in lakes having experienced the least amounts of development. Development activities expose and disturb soils and bedrock, facilitating the release of these constituents to nearby surface waters (Gorham et al. 1986; Fox et al. 1997; Potasznik and Szymczyk 2015; Tarr and White 2016; Kaushal et al. 2017). Another known anthropogenic source of base cations is WWTF effluent, which is known to discharge into three study lakes directly and another four indirectly, supporting that WWTF inputs of calcium may be driving the observed increase in calcium concentrations

(Potasznik and Szymczyk 2015; Kaushal et al. 2017). Additionally, these findings indicate that sulphate concentrations are declining in lakes where atmospheric inputs are the dominant source of sulphate, as opposed to those primarily influenced by acid rock drainage which can be exacerbated by urban development (Gorham et al. 1986; Tarr and White 2016).

A significant ($p < 0.01$) univariate model was also identified between ΔTP concentration and the level of development within the watersheds in ~1980 (Table 2.2). This positive relationship explained 17% of the variability in ΔTP and indicates that lakes that experienced the greatest increases in TP had the most developed watersheds in ~1980 and can likely be attributed to urban sources of nutrients (Ginn et al. 2015).

Changes in color over the ~30-year period (1991 – 2021) had a positive relationship with the flushing rate proxy, and a negative relationship with the level of watershed development in ~1980 (Table 2.2). Similarly, the best model for ΔDOC over the ~20-year period (2000 – 2021) revealed a positive relationship with the flushing rate proxy as well as wetland area (Table 2.2). Interestingly, although ΔDOC had a negative univariate relationship with road density (adj. $R^2 = 0.13$, $p < 0.01$), this variable does not appear in the final model (Table 2.2). These results suggest that lakes with the greatest increases in color and DOC were the least developed (typically coinciding with those having the lowest road density), had the largest watersheds relative to their surface area, and had the greatest proportion of wetlands within their watersheds. Since organic soils are the primary source of DOC to surface waters, increases in DOC (and accompanying increases in color) can be expected in lakes draining the largest watersheds relative to their surface area (Gorham et al. 1986). Additionally, less developed watersheds tend to have more wetlands and forested areas and thus contain larger stores of DOC (Gorham et al. 1986).

2.5.4 Climate change influences

The examination of temperature and precipitation trends in the months leading up to each synoptic survey reflect the observed increase in air temperature over the study period and the lack of linear trends in total precipitation since ~1980 (Fig. A.7). None of the periods stand out as particularly anomalous; however, the mean minimum temperature of the 6-

month period prior to the 2021 survey is notably > 1°C higher than that of 2011 (Fig. A.7). This may, in part, explain the minor (i.e., not statistically significant) decrease in chloride concentration and related constituents (i.e., sodium and conductivity) observed from 2011 to 2021, since there may have been less road salt applied during the warmer winter leading up to the 2021 survey (Fig. A.7).

Although testing the relationship between air temperature increases and changes in individual parameters went beyond the scope of this research, it is important to note that the observed increases in DOC, iron, and color within the study lakes could be related to temperature increases, since rising temperatures are known to increase the leaching of DOC and iron from soils (Harrison et al. 2008; Clair et al. 2011; Sarkkola et al. 2013). Further increases in these constituents are likely to occur in the years to come as temperatures are projected to continue rising, as is the frequency of extreme precipitation events that exacerbate the release of DOC and iron from soils (Harrison et al. 2008; Clair et al. 2011; Sarkkola et al. 2013; NSECCU 2014).

2.5.5 Limitations of the decadal spring synoptic monitoring method

The decadal nature of the SWQS between 1980 and 2021 limited the detection of linear trends in parameters given between three and five observations exist. Examination of a select set of plots illustrates the absence of significant linear trends despite substantial changes in water quality of some parameters over the study period (Fig. 2.6).

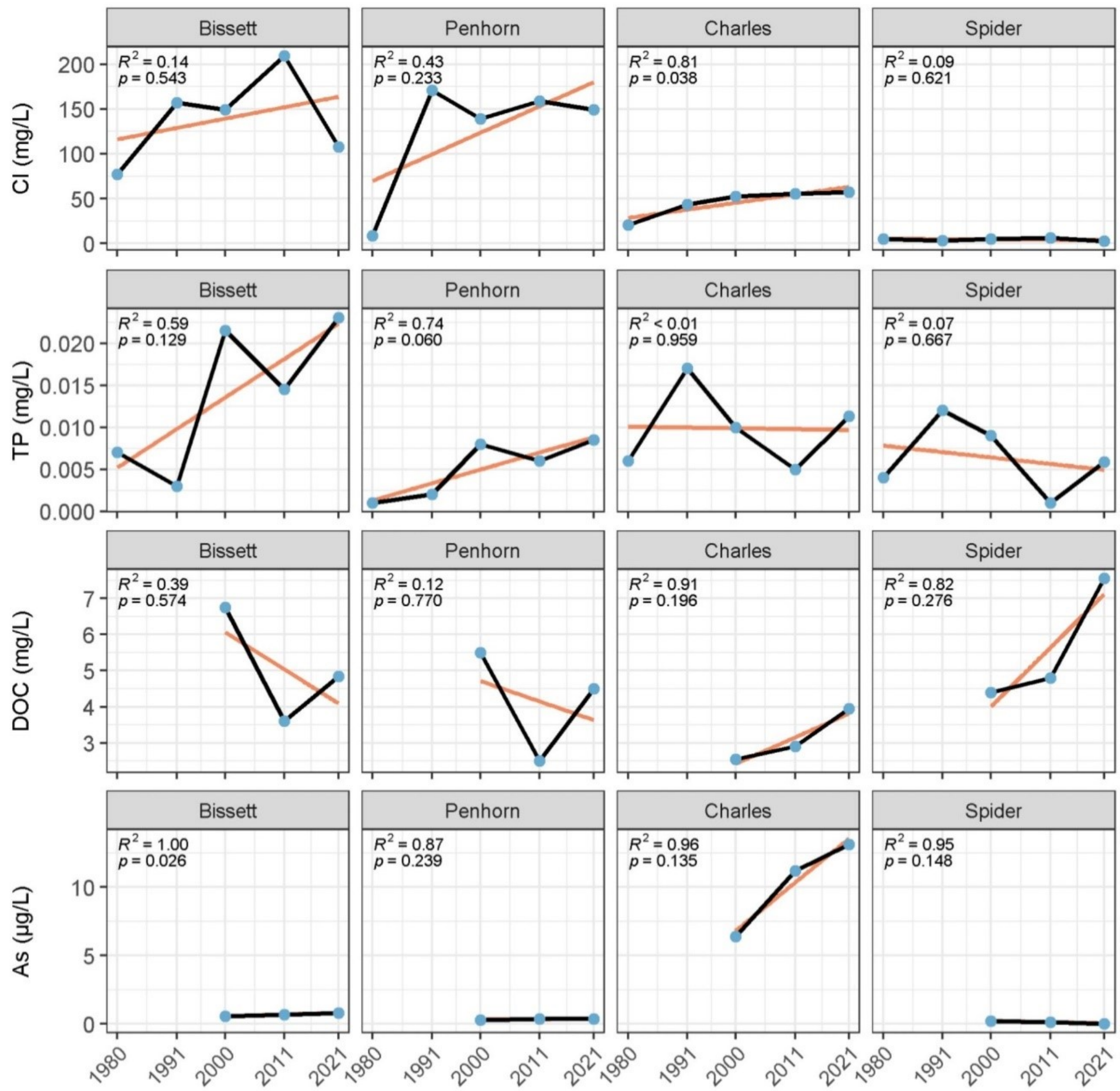

Figure 2.6. *Example of line plots with results of linear trend analysis (presented in Fig. A.3a-v) for the following lakes: Bissett, Penhorn, Charles, and Spider, for the following parameters: chloride, TP, DOC, and arsenic. Trendlines depicted in red. The lines connecting points (black) were included to emphasize patterns and trends (or lack thereof) and should not be interpreted as interpolating concentrations between surveys.*

Of the four lakes presented, Lake Charles is the only lake exhibiting a significant increase in chloride, despite the elevated concentrations observed in the more heavily developed Bissett and Penhorn lakes (Fig. 2.6). Increasing trends in TP can also be observed in Bissett and Penhorn, but neither trend is statistically significant (Fig. 2.6). This is also apparent for DOC in Lake Charles and Spider Lake, and for arsenic in Lake Charles, where examination suggests that these constituents are increasing but no significant linear trends are detected (Fig. 2.6).

2.6 Conclusion

Significant directional changes in lake water quality have occurred within HRM lakes over the past 40 years. As of 2021, national guidelines for the protection of aquatic life were exceeded by the concentrations of chloride in 20% of the lakes, aluminum in 29% of the lakes, manganese in two lakes, and arsenic in one lake. Since 1980, increases in major ions, trace elements, nutrients, pH, and organic matter were observed in the majority of the study lakes. Lakes with the greatest levels of urban development in their watersheds experienced the most pronounced increases in TP and major ions, such as chloride and calcium. Urban development appears to be a major driver of increased chloride, TP, and calcium concentrations, while increases in color and DOC concentrations appear to be influenced by hydrology and watershed characteristics. Decreasing acid deposition may partially explain recent increases in DOC, calcium, alkalinity, and pH, however anthropogenic factors are also likely to be significant contributors. Increasing temperatures and extreme precipitation events associated with climate change may be mobilizing DOC and iron in watershed soils, also contributing to increases in color that have been observed in many of the study lakes.

Our findings demonstrate that the spring synoptic sampling approach to water quality monitoring is most effective at highlighting broad trends, particularly in parameters that are more stable, while parameters that are more variable, such as nutrients, may require more intensive monitoring approaches with higher spatial and temporal resolutions. Our findings will help guide future studies by highlighting where trends may exist and identifying possible causes. This study has also brought greater attention and understanding to emerging water quality concerns, particularly the increases in chloride, aluminum, and arsenic concentrations in several lakes, that should be targeted within future sampling efforts.

CHAPTER 3 – TRACKING TROPHIC STATE IN URBAN LAKES IN A CHANGING CLIMATE: ARE EXISTING MONITORING PROTOCOLS STILL EFFECTIVE?

3.1 Abstract

Increasing eutrophication risk worldwide underscores the importance of identifying effective lake trophic state monitoring strategies for the preservation of lakes and the many environmental, cultural, and economic services they provide. The Organization for Economic Cooperation and Development (OECD) Cooperative Programme on Eutrophication identified phosphorus (P) as a key nutrient driving lake productivity and developed trophic state models in the 1970s that remain widely used to inform eutrophication management efforts. Given the changes in climate that have occurred since the 1970s and the diversity of lakes not represented in the original program, this study sought to reassess the applicability of the OECD's total phosphorus (TP)-chlorophyll *a* (Chl *a*) relationship in a set of diverse urban lakes. Further, this study aimed to assess the continued use of total phosphorus (TP) as a trophic state indicator, and to evaluate cost-effective approaches for characterizing TP in urban lakes. Trophic state parameters were tracked over the 2021 open-water season in fifteen lake basins in the Halifax Regional Municipality (HRM), Atlantic Canada, to examine relationships among productivity, nutrient dynamics, thermal stratification, and hypolimnetic anoxia. TP-Chl *a* relationships within fourteen of the fifteen study lakes were consistent with that of the original OECD models. Evidence of internal P loading was observed to varying degrees in twelve basins and appeared to be influenced by water chemistry, including chloride concentration, water color, and dissolved organic carbon concentration. TP concentrations in spring surface samples aligned closely with those measured throughout the ice-free season, with the exception of three lakes having complex nutrient cycling regimes. These results reveal that annual sampling during spring overturn may be sufficient to accurately characterize lake nutrient levels in many lakes, and broadly, indicate that TP concentration remains a reliable, cost-effective indicator for monitoring trophic state in diverse urban lakes.

Keywords: chlorophyll *a*, eutrophication, nutrient loading, OECD, phosphorus, productivity, trophic status

3.2 *Introduction*

Increasing eutrophication of surface waters driven by elevated nutrient loading from anthropogenic sources is observed worldwide (Vollenweider and Kerekes 1982; Schindler and Vallentyne 2008). This degradation of water quality has both socio-economic and ecological consequences, diminishing the recreational value of water bodies, increasing source water treatment costs (due to rapid fouling of filters and increased chemical demand), and creating inhospitable conditions for native biota such as through reduced clarity, depleted oxygen levels, and the release of toxins, resulting in fish kills, loss of habitat, and trophic cascades (Schindler and Vallentyne 2008; Chislock et al. 2013; Carmichael and Boyer 2016). Anthropogenic climate change can also exacerbate eutrophication by creating favorable conditions for algal blooms (Moore et al. 2008; Paerl et al. 2011; Pick 2016; Summers et al. 2016; Chapra et al. 2017). In lakes, air temperature increases result in surface water warming, decreased ice cover duration, as well as the strengthening and extension of thermal stratification (Moore et al. 2008; Nürnberg 2009; Paerl et al. 2011; Woolway et al. 2020). Additionally, increasing air temperatures coupled with more frequent extreme precipitation events accelerate the export of constituents such as DOC, iron, and nutrients from within watersheds (Harrison et al. 2008; Sarkkola et al. 2013). Importantly, these effects drive a shift from benign blooms to harmful algal blooms (HABs) often dominated by cyanobacteria that may have adverse health effects to humans and other organisms (Moore et al. 2008; Paerl et al. 2011; Pick 2016; Chapra et al. 2017).

The Organization for Economic Co-operation and Development (OECD) Cooperative Programme on Eutrophication was initiated in the 1960s to address increasing eutrophication risk worldwide and primarily aimed to characterize the relationship between nutrients and trophic response (using chlorophyll *a* as a proxy of algal biomass) in lakes. This was accomplished by analyzing data largely gathered from temperate, eutrophic lakes across 18 countries. A key finding of the OECD was that phosphorus (P) is typically the limiting nutrient in freshwater lakes, and could be used as a predictor of trophic state (Vollenweider and Kerekes 1982). The applicability of the OECD findings was evaluated in lakes across Canada in a separate report (the Canadian Contribution) in 1981 (Janus and Vollenweider 1981). In general, the statistical relationship between nutrient concentrations and trophic response in the Canadian study lakes was similar to the original OECD lakes. However, there were some inconsistencies in sampling methodology in the Canadian study, and lakes sampled for the Canadian contribution were primarily undeveloped and oligotrophic, leaving the applicability of these results to urban lakes in Canada unclear (Janus and Vollenweider 1981). In Canada, national guidelines for eutrophication management have been produced which rely on total phosphorus (TP) as the key indicator of trophic state in freshwater systems (CCME 2004). In this guideline, the original trophic state classification system proposed by the OECD was amended by the subdivision of the "meso-eutrophic" category (10 – 35 μg/L) into "mesotrophic" and "meso-eutrophic" categories (10 – 20 μg/L and 20 – 35 μg/L, respectively) to account for the diversity of Canadian lakes that fall within the range of the original category (CCME 2004). A table summarizing these ranges can be found in Table B.1. This classification system is widely used, including by the Halifax Regional Municipality (HRM) in Nova Scotia, Canada, to evaluate eutrophication risk and for the management and planning of new developments (HRM 2016).

The use of TP as a trophic state indicator has several advantages over chlorophyll *a* (Chl *a*), despite Chl *a* being a more direct measure of lake productivity, as TP is less challenging to measure, being less spatially and temporally variable (Cloutier and Sanchez 2007; Pasztaleniec 2016). However, various factors, including water temperature, nutrient availability, alkalinity, and morphological factors such as mean lake depth, turbidity, water clarity, and elevation, influence the strength of the relationship observed between TP and Chl *a* (Spears et al. 2013; Quinlan et al. 2021; Hoyer and Canfield 2022). Chloride ion concentrations are also known to affect lake productivity as a result of their influence on internal P loading (Novotny and Stefan 2012) and aquatic food webs (Hintz et al. 2017; Dugan et al. 2017; Fournier et al. 2021; Hébert et al. n.d.). Increasing salinity strengthens and extends the duration of thermal stratification, exacerbating dissolved oxygen (DO) depletion in the hypolimnion and creating an anoxic environment that favors the release of P from the sediment (Novotny and Stefan 2012; Radosavljevic et al. 2022). As a result, lakes affected by increasing chloride concentrations may not respond as well to P-management efforts that reduce external P loading (Novotny and Stefan 2012; Radosavljevic et al. 2022). Eutrophication itself is also capable of increasing productivity as microbial decomposition following an algal bloom further depletes hypolimnetic DO and thus reinforces internal P loading (Correll 1998). Conversely, elevated flushing rates may suppress lake productivity by removing algal cells and affecting nutrient retention, and have found to be negatively correlated with algal blooms (Kerekes 1975; Jones and Elliott 2007; Londe et al. 2016; Hoyer and Canfield 2022).

The impact of water color and dissolved organic carbon (DOC) concentration on productivity is more ambiguous, and both negative and positive relationships with productivity have been observed (Carpenter et al. 1998; Fergus et al. 2016; Hoyer and Canfield 2022; Tammeorg et al. 2022). These relationships tend to be highly variable, spatially dependent, and may also be influenced by factors such as mixing regime (Grzybowski 2014; Fergus et al. 2016). Frequently, color and DOC have been found to suppress productivity, and this has largely been attributed to light limitation and/or decreased nutrient bioavailability (Jones et al. 1988; Jones 1992; Carpenter et al. 1998; Thrane et al. 2014; Stetler et al. 2021; Hoyer and Canfield 2022). TP thresholds for increases in algal biomass are found to be higher in humic lakes (> 30 TCU) compared to their oligohumic counterparts (< 30 TCU), a phenomenon that has been attributed to the binding of humic substances to P in the hypolimnion when in the presence of iron (Jones et al. 1988; Carvalho et al. 2011; Vuorio et al. 2020). Further, elevated hypolimnetic DOC concentrations may negatively affect internal P loading as humic substances inhibit the release rate of iron-bound P within the sediment (Tammeorg et al. 2022). Conversely, studies have observed a positive relationship between color, DOC, and lake productivity (Fergus et al. 2016; Senar et al. 2021; Tammeorg et al. 2022). This is largely attributed to the concurrent influx of nutrients that are bound to DOC (e.g., N, P) and the increased internal warming resulting from light absorption nearer the lake’s surface (Senar et al. 2021; Isles et al. 2021; Fonseca et al. 2022; Puts et al. n.d.). Additionally, at low concentrations, the protection DOC provides from harmful UV is believed to have a positive effect on algal cells, particularly in shallow, high elevation lakes that are more vulnerable to UV transmission (Morris et al. 1995; Carpenter et al. 1998).

Regional and global scale environmental change is also altering lake systems, and potentially the applicability of trophic state classification systems developed decades ago. Increasing temperatures and extreme precipitation events may exacerbate nutrient loading and create more favorable growth conditions for primary producers such as cyanobacteria (Moore et al. 2008; Paerl et al. 2011; Pick 2016). Air temperatures in the HRM have increased by ~1°C over the last 40 years (Doucet et al. In Review) and are projected to increase by > 2°C by 2080 (NSECCU 2014). Total annual precipitation has not increased significantly over the last four decades (Doucet et al. In Review) but a ~7% increase is projected over the next 60 years in the region (NSECCU 2014). Additionally, changes in precipitation patterns are expected to accompany climate change in the region (i.e., increased extreme precipitation events) (NSECCU 2014). Many lakes in the northern hemisphere are also experiencing lake brownification, a phenomenon observed across the northern hemisphere that has been linked to climate change and acid deposition recovery, characterized by increasing water color and DOC concentrations (Evans et al. 2005; Skjelkvåle et al. 2005; Roulet and Moore 2006; Redden et al. 2021; Doucet et al. In Review).

Great diversity exists in the morphological and water quality characteristics of the over 1,000 lakes that are located within the HRM. Due to the increasing risk of eutrophication globally, and the ecological, economic, and recreational importance of lakes within the municipality, a cost-effective method of monitoring lake trophic state is needed. Historically, HRM has used TP as the key indicator of trophic state of lakes in the region, operating on the assumption that the relationships between TP and productivity (based on Chl *a* concentration) identified by the OECD in the 1970s-1980s are still applicable, despite shifts in climate and lake water quality (e.g., brownification, salinization) observed in the region (HRM 2016). These assumptions must be evaluated to ensure the efficacy of eutrophication monitoring in the municipality and to inform future management efforts. Therefore, this study sought to address the following questions:

1. What level of sampling/monitoring is required to adequately characterize the temporal and spatial dynamics of TP concentrations in diverse urban lakes? And does water chemistry appear to influence these dynamics?

2. Are existing trophic state relationships applicable in lakes that have been altered by both local (urbanization) and regional (climate, acid deposition) environmental change processes?

3.3 Study site

The study lake basins vary in size, location, watershed characteristics, and water quality (Fig. 3.1, Tables 3.1, 3.2). They were selected from a group of ~50 lakes that have been the focus of the Synoptic Water Quality Study (SWQS) of select HRM lakes (Clement et al. 2019; Doucet et al. In Review), with the exception of Fish Lake, which was added to the subset over the summer monitoring period to assist with evaluating the applicability of OECD relationships to a more diverse range of HRM lakes (Fig. 3.1).

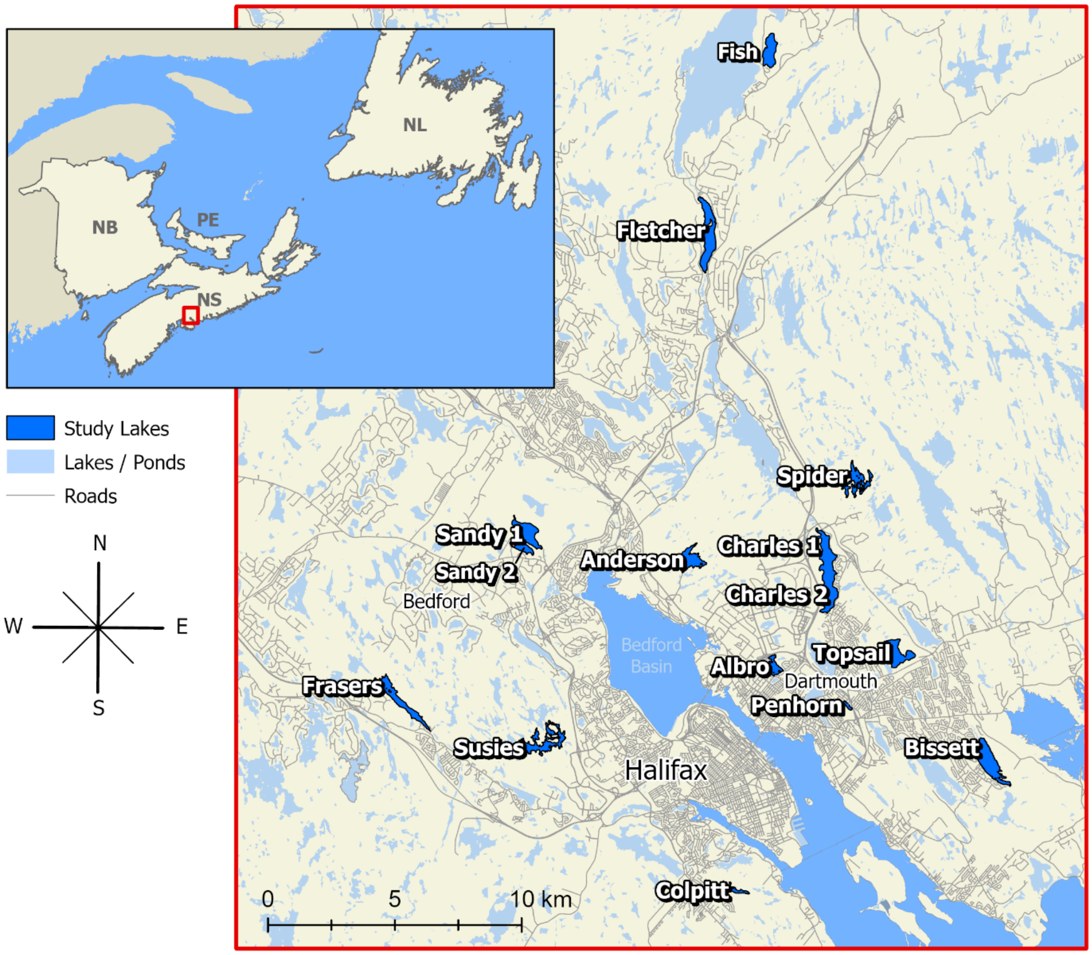

Figure 3.1. *Map depicting study lakes, with both basins of Lake Charles and Sandy Lake indicated (dark blue), other water features (light blue), and road network (grey lines). Inset: study area situated in Atlantic Canada. Map projection: NAD 1983 UTM Zone 20N. Map data sources listed in Table B.2.*

Topsail Lake is the shallowest, having a maximum depth of 7 m, while Lake Charles is the deepest, having a maximum depth of ~30 m (Table 3.1). Penhorn Lake is the smallest in terms of surface area and volume, at 0.04 km^2 and ~125,000 m^3, respectively, while Lake Charles is the largest, having a surface area of 1.4 km^2 and a volume of ~12,000,000 m^3 (Table 3.1; Fig. 3.1). Lake watersheds ranged from 0.2 km^2 (Penhorn) to 141.4 km^2 (Fletcher) (Table 3.1), while exposure to urban development ranged from < 1% to > 60% of the watershed developed as of 2020 (Table 3.1). Development projects are slated to occur within the watersheds of Penhorn Lake (HRM 2022), Sandy Lake

(Province of Nova Scotia 2022c), and Lake Charles (Province of Nova Scotia 2022b), and construction is already underway on the Highway 107 extension intersecting Anderson Lake's watershed (Nova Scotia Public Works 2021).

Table 3.1. *Lake basin morphometry and lake watershed characteristics for 14-lake basin subset of Synoptic Water Quality Study (SWQS) lakes. *Metrics apply to the combined Susies Lake and adjacent Quarry Lake watershed that was used in Doucet et al. (In Review) for consistency with the SWQS.*

	Maximum Depth (m)	Basin Volume (m^3)	Basin Surface Area (km^2)	Watershed Area (km^2)	Watershed Development (%)
Albro	8	434,875	0.23	0.9	40.9
Anderson	26	4,907,093	0.62	4.9	19.7
Bissett	10	2,190,918	0.89	7.9	61.0
Charles 1	30	9,719,050	1.00	20.8	30.5
Charles 2	14	2,282,714	0.41		
Colpitt	12	442,764	0.15	2.3	31.4
Fletcher	11	2,320,641	1.01	141.4	17.0
Frasers	20	5,039,336	0.67	38.5	12.5
Penhorn	9	126,552	0.04	0.2	56.8
Sandy 1	21	4,986,056	0.55	18.0	22.6
Sandy 2	6	513,911	0.19		
Spider	10	1,387,359	0.63	5.9	0.9
Susies	10	2,358,529	0.82	13.6*	10.0*
Topsail	7	2,314,462	0.61	2.2	8.0

Wastewater in the HRM is treated either at wastewater treatment facilities (WWTF) as part of the municipal sewer system or through residential septic systems. Lake Fletcher is the only study lake that is affected by WWTF effluent, receiving effluent from three WWTFs, including from one directly and two indirectly (Table A.2). All three facilities utilize tertiary treatment (Table A.2).

The study lakes range from acidic to near neutral, with Susies Lake being the most acidic, having a pH of 4.8, and Penhorn Lake the most alkaline at a pH of 7.6 (Table 3.2). HRM lakes are naturally acidic, and it is believed that few lakes would have exceeded a pH of 6 prior to the 20th century (Ginn et al. 2015; Clement et al. 2019). The lakes range from ultra-oligotrophic to meso-eutrophic based on the CCME Trophic State trigger ranges (2004), with the lowest TP concentration found in Topsail Lake at 3 μg/L, and the highest concentration in Bissett Lake at 23 μg/L (Table 3.2).

Identifying the limiting nutrient or environmental factor is crucial to develop effective lake management strategies. When lakes are not P-limited, or when P is not the limiting environmental factor, empirical eutrophication models (such as the OECD relationship) may not be applicable and should not be relied upon to understand how changes in P loading affect water chemistry and trophic state (Hoyer and Canfield 2022). Optimal TN:TP ratios for freshwater primary producers are known to vary by species, however, N-limitation may occurs at atomic ratios of TN:TP < 10 (Schanz and Juon 1983; Hoyer and Canfield 2022), by which definition none of the study lakes are N-limited (Table 3.2). However, N-deficient growth has been observed in other studies at atomic ratios as high as 20 (Guildford and Hecky 2000) and even 30 (Rhee 1978; Downing and McCauley 1992), suggesting that Frasers, Penhorn, and Albro may be considered N-limited, having ratios of 26, 26, and 36, respectively (Table 3.2). These three, along with Topsail Lake, had TN concentrations near or below the detection limit (Table 3.2). Proposed thresholds for P-limitation are similarly variable, ranging from TN:TP > 16 (Redfield 1958; Klausmeier et al. 2004) to TN:TP > 50 (Guildford and Hecky 2000). By the former definition, all of the study lakes can be considered P-limited, while the latter definition would exclude Frasers, Penhorn, and Albro (Table 3.2).

Table 3.2. *Water quality characteristics measured during the 2021 Synoptic Water Quality Study survey (Doucet et al. In Review). *Measurements from Susies Lake were averaged with those from the adjacent Quarry Lake.*

	pH	TP (µg/L)	TN (µg/L)	TN:TP atomic ratio	Color (TCU)	DOC (mg/L)	Iron (µg /L)	Chloride (mg/L)
Albro	7.1	6	< 100	36	< 5	3	66	102
Anderson	5.9	6	300	116	26	5	137	10
Bissett	7.4	23	750	72	21	5	211	108
Charles	7.2	11	400	78	12	4	56	58
Colpitt	6.3	8	1200	320	66	10	170	82
Fletcher	6.4	13	733	129	47	6	205	16
Frasers	5.3	11	125	26	55	8	180	15
Penhorn	7.6	8	< 100	26	5	4	67	149
Sandy	6.6	10	700	147	31	6	387	41
Spider	5.1	6	300	112	19	8	172	3
Susies Quarry*	4.8	6	350	125	44	7	132	36
Topsail	5.9	3	< 100	65	11	3	47	13

The study lakes range from clear to highly colored, with Penhorn and Albro being the clearest, falling at and below the detection limit, respectively, and Colpitt (66 TCU) and Frasers (54 TCU) being the most colored (Table 3.2). Similarly, the highest DOC concentrations were observed in Colpitt and Frasers at 10 mg/L and 8 mg/L, respectively, while the lowest concentrations of DOC were observed in Albro and Topsail at 3 mg/L (Table 3.2). Iron concentrations ranged from 47 µg /L in Topsail Lake to 387 µg /L in Sandy Lake (Table 3.2). The highest chloride ion concentration was observed in Penhorn Lake at 149 mg/L, while the lowest was observed in Spider Lake at 3 mg/L (Table 3.2). Increasing chloride ion concentrations are largely attributed to road salt application and have been identified as a water quality concern in HRM lakes (Ginn et al. 2015; Clement and Gordon, 2019; Doucet et al. In Review).

3.4 Materials and methods

3.4.1 Data and sample collection

Lake morphometric data was collected from multiple sources. Spring turnover surface TP and Chl *a* concentrations were obtained from the 2021 SWQS survey and these methods are described in detail in Doucet et al. (In Review), along with details regarding watershed delineation and the quantification of watershed development levels. Spring turnover surface concentration data does not exist for Fish Lake as it does not belong to the SWQS dataset. An additional four sampling events were performed over the open water season of 2021, including a May/June session (May 14, 2021, to June 8, 2021) that aimed to capture weak spring stratification, a June/July session (June 22, 2021, to July 8, 2021), an August session (August 16, 2021, to August 23, 2021) that aimed to capture peak stratification, and a fall overturn session (October 6, 2021, to December 1, 2021).

For the first three sampling sessions, a YSI Model 600 sonde (YSI Inc., Yellow Springs, OH, USA) was submerged at the deepest point in each basin to collect temperature, pH, and DO (% saturation and mg/L) measurements at regular intervals throughout the water column. Secchi depth was measured and used to estimate photic zone depth (2.5 × Secchi depth) (USGS 2018). Water samples were collected using a Kimmerer sampler and were transferred to clean plastic containers. Samples for TP were typically collected at five depths including one from the surface, one from the bottom of the epilimnion, one from within the thermocline, one from the top of the hypolimnion, and one just above the sediment-water interface. Samples for Chl *a* were collected at four depths including one from the surface, one from the Secchi depth, one from 1 m below the Secchi depth, and one from the bottom of the photic zone. During the final sampling session (October to December), a temperature profile was collected at the deepest point in each basin to determine if the basin had mixed, and only surface water TP and Chl *a* samples were collected from lakes that were no longer stratified. All water samples were stored in a cooler on ice during transport to the laboratory where they were refrigerated until ready for analysis. Where possible, water samples were either processed within 24 hours or frozen at -20°C for later analysis.

3.4.2 Sample processing

All samples were measured in duplicate, and blanks were used for quality control and quality assurance. TP was analyzed at Dalhousie University by digesting samples as per Menzel and Corwin (1965) and measuring P through the ascorbic acid method (Murphy and Riley 1962) on a 100 mm pathlength cell at 880 nm (detection limit of 1 µg/L) in a HACH DR-5000 spectrophotometer (HACH, Loveland, CA, USA). Chl *a* samples were analyzed by the Oceanography Department at Dalhousie University through both a fluorometric acidification method (as per Yentsch & Menzel (1963); modified by Holm-Hansen et al. (1965); recommended by Strickland & Parsons (1968)) as well as an approach developed by Welschmeyer that minimizes the interference from Chlorophyll *b* and pheopigments (1994). The results from the two methods were generally in agreement. Results from the Welschmeyer method are presented herein, except where Welschmeyer results were not available due to equipment failure, where the acidification results have been substituted.

3.4.3 Data analysis

Depth profiles depicting temperature, DO, and TP from the August sampling session (peak stratification) were plotted on a common depth axis to show relative depth of each study lake and were created in R (Version 4.1.2). All other plots were created in Microsoft Excel (Version 2201).

Several TP concentration metrics were calculated for each of the SWQS lake basins (all but Fish Lake) from measurements collected during the May/June sampling session (early stratification) and August sampling session and compared to the synoptic spring surface TP concentrations (TP_{syn}). These included the arithmetic mean concentration in the epilimnion (TP_{epi}), hypolimnion (TP_{hyp}), photic zone (TP_{pz}), and entire basin (TP_{avg}), as well as the volume-weighted concentration for the entire basin (TP_{vw}). The total volume of each basin and the volume of the stratum corresponding to each TP measurement was required for the calculation of TP_{vw}. These values were determined by modelling each lake basin using a Triangulated Irregular Network (TIN) derived from digitized and georectified (1st order polynomial transformation or spline transformation) bathymetry contour lines in ArcGIS Pro 2.7.3. This method yields more accurate results compared to the commonly used cone frustum volume method (Wetzel and Likens 2000; Hollister and Milstead 2010). Each basin was divided into strata based on the depths at which TP measurements were collected such that planes dividing the model were located halfway between the depth of each TP measurement.

The applicability of the TP-Chl *a* relationships established by the OECD to the study lakes was evaluated by calculating the arithmetic mean photic zone TP concentration and Chl *a* concentration for the ice-free season in its entirety (synoptic surface concentrations were averaged with the mean photic zone concentration for each of the four sampling sessions) and plotting them on log-log axes against the 80th and 95th confidence intervals of the OECD relationship. The findings of the OECD programme were intended to describe the statistical behaviour of certain types of lakes and not to predict trophic response in individual lakes, and as such, agreement with the OECD relationships has historically been evaluated by plotting lakes against 80% and 95% confidence intervals (Janus and Vollenweider 1981). Test case values that fall within the 80% limits are deemed to conform with the OECD relationship (Janus and Vollenweider 1981). Those values falling between the 80% and 95% limits are suspected of being non-conforming, while those outside the 95% limits are deemed to not conform with the OECD relationship (Janus and Vollenweider 1981). For this analysis, data from Fish Lake (not part of the SWQS) was included, however as Fish Lake was not sampled immediately following ice-out or during the first sampling session, the TP and Chl *a* metrics are based solely on data collected during the last three sampling sessions.

3.5 Results and discussion

3.5.1 Depth profiles: temperature, DO, and TP among lake basins

As of August (peak stratification), all study lakes with the exception of Topsail Lake were stratified (where thermal stratification is defined as a temperature change of > 1°C within 1 m) (Fig. B.1). Expectedly, stratification was weak or absent in shallow lakes with greater exposure to wind (i.e., longer fetch relative to maximum depth) and stronger in deeper lakes and those having less wind exposure, such as those with smaller surface areas relative to their maximum depth and those of irregular shapes. Albro, Bissett, Fletcher, and Sandy 2 were weakly stratified (Fig. 3.2; Fig. B.1), while strong thermal stratification was observed in Spider, Susies, Anderson, Colpitt, Frasers, Sandy 1, Charles 1, Charles 2, and Penhorn (Fig. 3.2; Fig. B.1).

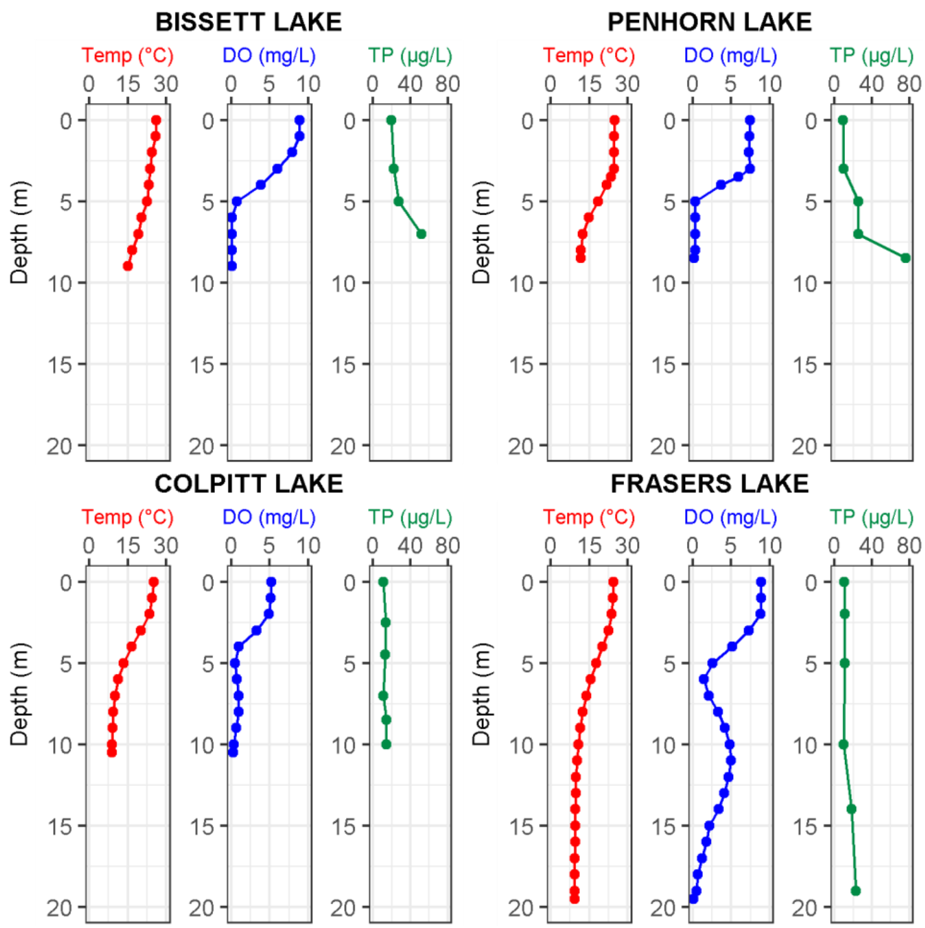

Figure 3.2. *Example depth profiles depicting temperature (°C; red), dissolved oxygen (DO; mg/L; blue), and total phosphorus (TP; µg/L; green) from the August sampling session (peak stratification) plotted on a common depth axis (20 m) to show relative depth of each basin.*

Hypolimnetic DO depletion was observed to some degree in all of the study lakes during peak stratification, but was minimal in Anderson, Charles 1, Spider, and Topsail Lake (Fig. B.1). Low productivity levels in Topsail, Anderson, and Spider could explain the minimal DO depletion observed (Doucet et al. In Review), as could their low chloride concentrations since elevated chloride strengthens stratification and thus exacerbates DO depletion (Table 3.2) (Novotny and Stefan 2012). As the strength and duration of thermal stratification influences hypolimnetic DO depletion, hypolimnetic anoxia (DO concentration of < 1 mg/L (Nürnberg 1995)) was expected in the eight basins having experienced the strongest stratification but was only observed in six, including Susies, Colpitt, Frasers, Sandy 1, Charles 2, and Penhorn (Fig. 3.2; Fig. B.1). Anoxic conditions were also observed in two of the lakes that were weakly stratified, including Bissett and Fletcher (Fig. 3.2; Fig. B.1). Anoxic layers ranged from 1 m thick in Charles 1 to 5 m thick in Bissett and Colpitt (Table B.3), accounting for between 7% and 50% of the entire water column depth in Charles 1 and Bissett, respectively (Table B.3). The lowest DO concentrations at the sediment water interface were observed in Fletcher and Bissett at 0.05 mg/L and 0.07 mg/L, respectively (Table B.3).

In Figure 3.2, depth profiles for four lakes (Penhorn, Bisset, Colpitt, and Frasers) that experienced hypolimnetic DO depletion, but displayed contrasting levels of internal P loading, are illustrated. The elevated hypolimnetic TP concentrations during peak stratification observed in both Penhorn Lake and Bissett Lake are indicative of internal P loading (Fig 2). It should be noted that the bottom-most sample from Bissett Lake was lost, and as such, the true TP concentration may have been much higher than reported (Table B.4). Penhorn Lake and Bissett Lake also had the highest chloride concentrations of the study lakes, at 149 mg/L and 108 mg/L, respectively (Doucet et al. In Review) (Table 3.2), which may have exacerbated DO depletion and subsequent internal P loading. Evidence of internal loading can also be observed in Fletcher, Sandy 1, Charles 2, Frasers, and Susies Lake (Fig. 3.2; Fig. B.1). Of the lakes exhibiting hypolimnetic anoxia during peak stratification, Colpitt Lake shows the least pronounced evidence of internal loading, followed by Frasers Lake (Fig. 3.2). Interestingly, Colpitt and Frasers are the most colored lakes having the highest DOC concentrations, which could indicate that internal P loading is being suppressed by the presence of humic substances, creating complexes with iron-bound P that diminish the rate at which P is released from the sediment (Tammeorg et al. 2022).

3.5.2 Comparison of different TP metrics and evidence of internal P loading

With the exception of Fletcher, Colpitt, and Penhorn, TP_{syn} concentrations aligned closely with the volume-weighted concentrations measured later in the growing season (Fig. 3.3). In Fletcher, the TP_{syn} concentration was higher than the TP_{vw} observed during both the

May/June and August sampling sessions and could be a result of Fletcher Lake's high flushing rate and large watershed (Fig. 3.3; Table 3.1). Conversely, the TP_{syn} concentration in Colpitt Lake was markedly lower than the TP_{vw} concentration observed during both the May/June and August sampling sessions, while in Penhorn Lake, the TP_{syn} concentration and May/June TP_{vw} concentration were similar but considerably lower than the TP_{vw} concentration observed in August (Fig. 3.3).

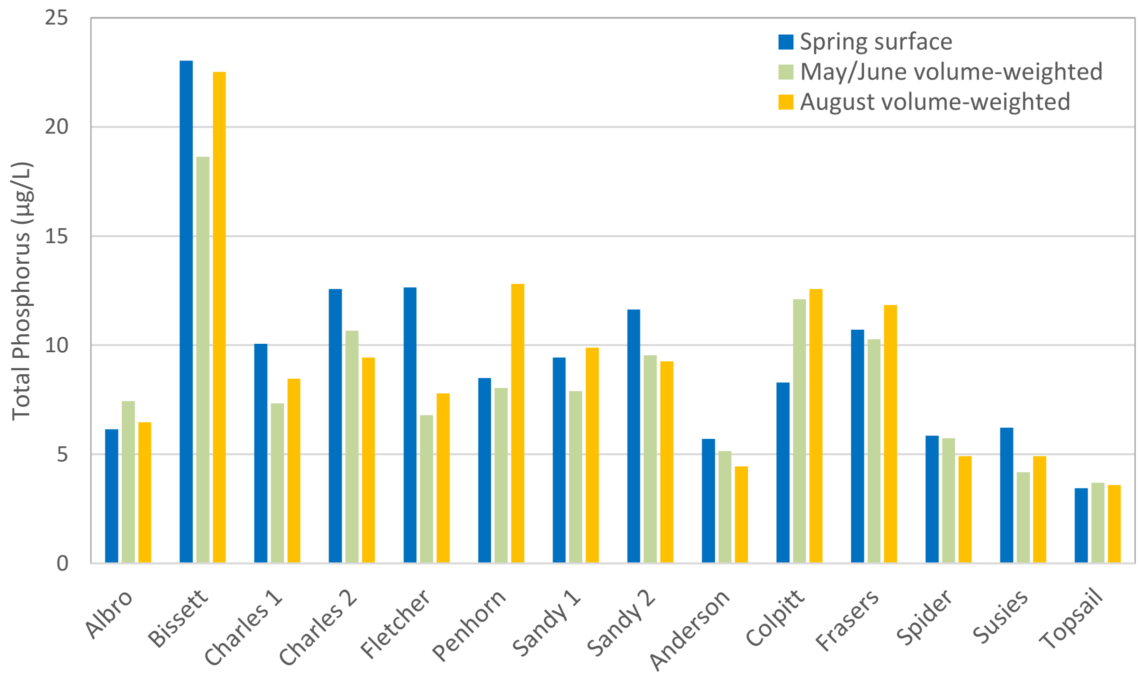

Figure 3.3. *Bar plot depicting spring surface sample total phosphorus (TP) concentrations (from the Synoptic Water Quality Study (SWQS); Doucet et al. In Review) in blue, volume-weighted TP concentrations from the May/June sampling session (light green), and volume-weighted TP concentrations from the August sampling session (yellow) for the fourteen study lake basins belonging to the SWQS.*

Due to the depletion of P through biological use over the growing season, TP_{syn} concentrations were expected to be the highest of the three metrics in most basins, however this trend was only observed in four basins, including Charles 2, Sandy 2, Anderson, and Spider (Fig. 3.3). Low biological activity likely accounts for the absence of this trend in Topsail Lake, as the three metrics aligned closely (Fig. 3.3). The majority of basins, including Bissett, Charles 1, Fletcher, Penhorn, Sandy 1, Frasers, and Susies, reflected an initial decline in TP concentration from the TP_{syn} concentration to the

May/June TP_{vw} concentration followed by an increase in TP during the August sampling, with the August TP_{vw} concentrations surpassing both the May/June TP_{vw} concentrations and the TP_{syn} concentrations in Penhorn, Sandy 1, and Frasers (Fig. 3.3). These results indicate that while spring surface sampling may adequately characterize nutrient levels in many of the study lake basins, it may fail to capture the complex nutrient dynamics present in certain lakes, such as those with high levels of internal loading. Of the eight basins that experienced an increase in TP_{vw} concentration from May/June to August, the greatest increase (> 50%) was observed in Penhorn Lake, with a pronounced increase also observed in Bissett Lake (Fig. 3.3). Many of these increases can be attributed to elevated TP concentrations within the hypolimnion in the late summer (Fig. 3.4).

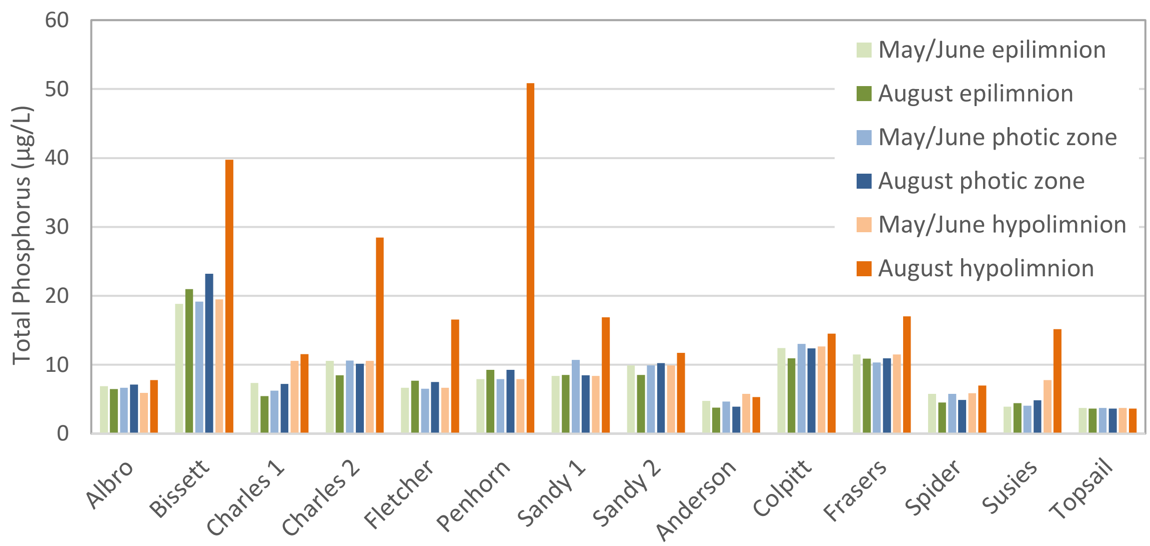

Figure 3.4. *Bar plot comparing various total phosphorus (TP) concentration metrics (µg/L) for the fourteen Synoptic Water Quality Study lake basins, including mean epilimnion concentrations in May/June (light green) and August (dark green), mean photic zone concentrations in May/June (light blue) and August (dark blue), and mean hypolimnion concentrations in May/June (light orange) and August (dark orange).*

Anderson Lake and Topsail Lake were the only basins within which hypolimnetic TP concentrations were not elevated during peak stratification (Fig. 3.4). The greatest increase in hypolimnetic TP was observed in Penhorn Lake, followed by Bissett and Charles 2 (Fig. 3.4). These elevated TP concentrations indicate that internal P loading is responsible for the observed increases in TP_{vw} over the summer months (Figs. 3.3, 3.4).

Moderate internal loading was observed in Fletcher, Sandy 1, and Susies Lakes, while minor internal loading was observed in the remaining basins (Fig. 3.4).

Biological depletion of P within the epilimnion over the growing season was observed in most lakes, with the exception of Bissett, Fletcher, Penhorn, Sandy 1, and Susies, where minor increases (< 3 μg/L) were observed (Fig. 3.4). The most pronounced increases were observed in Bissett Lake and Penhorn Lake, within which the strongest evidence of internal P loading was also observed, indicating that some degree of P transfer may be occurring from the hypolimnion to the epilimnion (Fig. 3.4). This transfer may be enabled by the relatively weak thermal stratification observed in Bissett Lake, and the use of aerators within Penhorn Lake that promote mixing (Fig. 3.2). Conversely, although Lake Fletcher also exhibited elevated hypolimnetic TP concentrations in August, Fletcher's high flushing rate could also explain elevated epilimnetic TP concentrations by bringing new P into the lake throughout the summer months (Fig. 3.4).

Although many lakes had minor increases in TP concentration within the photic zone over the growing season (the largest being a 4 μg/L increase observed in Bissett Lake), concentrations did not increase markedly during peak stratification even in lakes experiencing high levels of internal loading, suggesting that the elevated concentrations are not available to photosynthetic organisms (Fig. 3.4). Lakes with high levels of internal loading are, however, at high risk of fall phytoplankton blooms once the hypolimnetic P is mixed throughout the water column.

3.5.3 Applicability of the OECD relationship (TP – Chl a)

Chl *a* peaked in the lakes at different times throughout the summer, with most basins experiencing a peak during the early summer and late summer sampling sessions (Table 3.3). Maximum Chl *a* concentrations were observed near the bottom of the photic zone in four of the 15 basins, with maximum concentrations observed near the Secchi depth in eight basins (Table 3.3). The highest concentration of Chl *a* was observed in Penhorn Lake in mid-October at 16 μg/L, while the lake remained stratified (Table 3.3). These results suggest that the high TP concentrations observed in the hypolimnion of Penhorn Lake in August may have caused an increase in productivity in the fall months as the thermocline began to erode. It should be noted that Penhorn Lake was resampled following fall mixing and the October measurement was excluded from the calculation of the mean growing season Chl *a* concentration for the sake of consistency (Table B.4).

Table 3.3. *Maximum Chl a concentrations observed in each basin over the summer sampling program. *Penhorn was sampled on October 14, 2021, as part of the fall sampling session however these results were excluded from all analyses as the basin was still stratified and was thus resampled on December 1, 2021.*

Lake	Date Collected	Sampling Session	Chl *a* (µg/L)	Sample Depth (m)	Photic Depth (m)
Fletcher	June 4, 2021	May/June	5	2.5	6.2
Charles 1	June 22, 2021	June/July	6	7	7.2
Charles 2	June 22, 2021	June/July	5	4	8.2
Albro	June 29, 2021	June/July	5	7	7.5
Penhorn	June 29, 2021	June/July	14	6	13.7
Sandy 1	June 29, 2021	June/July	3	0	7.7
Sandy 2	June 29, 2021	June/July	23	3	7.5
Fish	July 6, 2021	June/July	12	4	4
Susies	July 8, 2021	June/July	2	3	6.9
Spider	August 16, 2021	August	2	3	4.9
Colpitt	August 18, 2021	August	10	2.5	2.7
Frasers	August 20, 2021	August	7	3	5.5
Anderson	August 23, 2021	August	4	5	7.7
Bissett	August 23, 2021	August	12	3	9.2
Penhorn*	October 14, 2021	Fall*	16	0	4.4
Topsail	October 12, 2021	Fall	1	0	12.7

Anderson Lake was the only basin that did not conform with the OECD TP-Chl *a* relationship, falling outside both the 80% and 95% confidence limits of the OECD line (Janus and Vollenweider 1981) (Fig. 3.5A). Similarly, when using the spring surface TP concentrations, Anderson Lake fell outside the 80% confidence limits, but within the 95% confidence limits, and is thus suspected of being non-conforming (Janus and Vollenweider 1981) (Fig. 3.5B). The remaining basins, regardless of the TP metric used, fell within the 80% confidence limits and appear to conform with the OECD relationship (Fig. 3.5A, B).

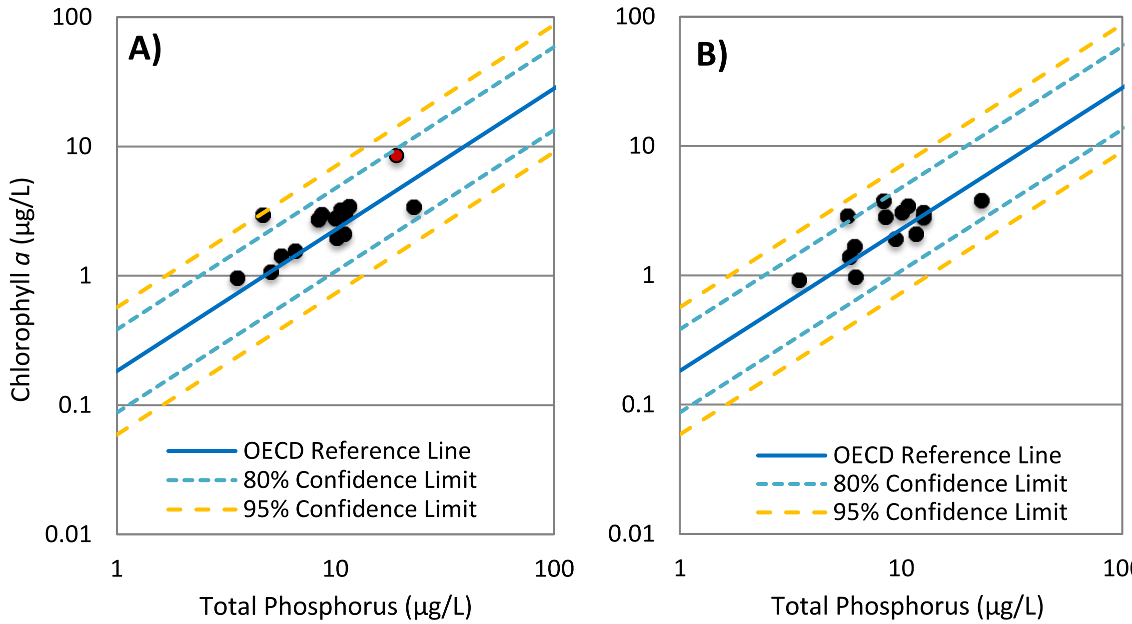

Figure 3.5. *The OECD reference line (solid blue) and 80% (dashed blue) and 95% (dashed yellow) confidence limits are plotted on a log-log scale along with the mean Chl a concentration over the growing season for each lake basin against the A) mean photic zone TP concentration over the growing season, and the B) spring surface TP concentration. Fish Lake is indicated in red.*

These findings indicate that, despite the variety in chemical and morphological characteristics of the study lakes, and the ~1°C increase in air temperature that has occurred in the region since the OECD relationship was established (Doucet et al. In Review), the OECD relationship remains representative of the statistical behaviour of the HRM study lakes. This is consistent with the findings of the Canadian contribution to the OECD, that evaluated the TP-Chl *a* relationship on oligotrophic lakes in undeveloped watersheds, including nine in Nova Scotia, and generally found the lakes to exhibit the same relationship between nutrient loads and trophic state as the original OECD lakes (Janus and Vollenweider 1981). They are also in accordance with the findings of a study by Kerekes et al. (1990) that tested a set of 20 acidic and non-acidic lakes in Nova Scotia and found them to be conforming within the OECD relationships regardless of pH (Kerekes et al. 1990). More recently, a strong relationship between TP and Chl *a*, consistent with the OECD relationship, was also identified by the Centre for Water Resources Studies (CWRS) in a set of 50 lakes within HRM, sampled between 2006 and

2011, which included Lake Fletcher, Lake Charles, Bissett Lake, Penhorn Lake, Albro Lake, and Sandy Lake (Stantec Consulting Ltd. 2012; CWRS 2016).

3.6 Conclusion

Current lake monitoring and management efforts in many urbanizing regions such as HRM rely on relationships between nutrient levels and productivity identified decades ago by the OECD, despite the shifts in climate and lake water chemistry that have been observed in many regions. As such, it is important to verify that these relationships remain applicable. As all but one of the study lakes in this study were found to be conforming with the OECD relationship, TP appears to remain a useful indicator of lake trophic state in urban lakes that possess varying water quality and morphological characteristics. This finding will support monitoring and management efforts as eutrophication risk continues to rise in surface waters around the globe. In general, spring surface sampling was effective for assessing lake trophic state. However, substantial internal P loading was observed in several lakes and resulted in marked increases in TP throughout the growing season. Lakes with suspected elevated internal loading should therefore be targeted for more detailed sampling within regional monitoring programs. Factors that should be considered for assessing potential for internal P loading include morphological characteristics such as maximum depth, wind exposure and flushing rate, but we also observed that lakes with elevated chloride concentrations and low DOC had the highest rates of internal P loading. However, this observation should be evaluated further in a larger set of lakes.

CHAPTER 4 – CONCLUSION

Water quality was evaluated in a large and diverse set of HRM lakes over a 40-year period, and trophic state parameters were tracked in a subset of these lakes over the 2021 open-water season. This thesis highlighted concerning concentrations of certain constituents and emerging trends in many lakes while exploring factors that could be driving these changes and evaluating monitoring methods to make recommendations for future research. The findings of Chapter 2 reveal that significant water quality changes have occurred in HRM lakes since the inception of the SWQS in 1980, including increases in major ions, trace elements, nutrients, pH, and organic matter in most of the study lakes. Increases in DOC, iron, color, alkalinity, and pH may, in part, be explained by regional factors such as decreased acid deposition and climate change. Watershed characteristics (e.g., wetland presence) and hydrology also appear to be important drivers of observed changes in parameters such as DOC and color. Urban development was identified as an important driver of the observed increases in TP and major ions (i.e., chloride and calcium), underscoring the importance of land use management to preserve lake ecosystems. Furthermore, Chapter 2 highlighted parameters that may be posing a risk to aquatic life in certain HRM lakes. In over 20% of the study lakes, concentrations of chloride and aluminum exceeded national guidelines for the protection of aquatic life, while two lakes had manganese concentrations above national guidelines and a single lake had an arsenic concentration above the national guideline. Chapter 2 further indicated that decadal spring synoptic sampling effectively highlights broad water quality trends and is particularly reliable when monitoring parameters exhibiting low levels of variability, while parameters having higher spatial and temporal variability (e.g., nutrients) likely require more thorough monitoring approaches.

Chapter 3 supports the continued use of TP as an indicator of lake trophic state in HRM, in accordance with OECD relationships adapted by the CCME, despite the diverse physical and morphological characteristics of HRM lakes and changes in climate that have occurred since these relationships were first identified in the 1970s. Further, this chapter highlighted the importance of identifying a lake's internal P loading potential to determine if spring synoptic surface sampling will be sufficient for characterizing nutrient levels as part of a lake monitoring program. In addition to physical characteristics such as depth, fetch, and flushing rate, chloride and DOC concentrations should be considered when attempting to determine lake internal P loading potential, as these constituents appeared to be influential within the study lakes. Due to the relatively small sample size used for this study, further research on a larger dataset is recommended to support these findings.

4.1 Recommendations for future research

This thesis primarily serves to inform and focus future research by highlighting emerging water quality concerns, identifying high-risk lakes, and evaluating the utility of different monitoring approaches. Further examination of the parameters exceeding national guidelines for the protection of aquatic life is recommended, including their causes, risk factors, and signs of negative effects on biota. This includes elevated aluminum concentrations, primarily in lakes affected by acid rock drainage, that may adversely affect various fish species at the concentrations observed in a number of the study lakes. The potential for increasing DOC concentrations to offset the effects of aluminum by mitigating its toxicity should also be explored. Particular attention should also be given to increasing chloride, given its wide-reaching influence and potential to exacerbate other water quality concerns (i.e., eutrophication). Additionally, the findings of this research support the continued examination of increasing arsenic concentrations in Lake Charles and identify nearby lakes where observed increases in arsenic may warrant investigation.

The increases in TP observed in lakes having developed watersheds emphasizes the need for effective and efficient future monitoring methods. Although spring surface sampling was found to be a relatively effective method of characterizing lake trophic levels, decadal sampling is likely insufficient due to the high variability observed among years. Annual spring surface sampling may be adequate for many of the study lakes, however those lakes experiencing high levels of internal loading likely require sampling at a higher temporal and spatial resolution. As such, efforts to determine the internal loading potential of lakes are recommended prior to the development of future monitoring strategies, accounting for factors such as elevated chloride, DOC and color. These parameters appear to have the potential to exacerbate or suppress internal loading, however this finding requires validation using a larger dataset.

The utility of the decadal spring synoptic sampling method for monitoring broad trends in water quality in a large set of lakes was supported by the results presented within this thesis and, as such, continuation of the SWQS is recommended in 2031. This will serve to further validate the efficacy of the method while also confirming or contradicting the possible trends identified as of 2021 by extending the time-series and allowing the use of more rigorous trend analyses.

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APPENDIX A – CHAPTER 2 SUPPLEMENTARY MATERIALS

Table A.1. *Table listing the synoptic samples collected, the lakes each was sourced from, and other notable information regarding each sample/lake.*

Lake #	Sample #	Lake English Name / Lake Mi'kmaw Name	Surface Area (km^2)	~Max. Depth (m)	~Volume (m^3)	~Water -shed Area (km^2)
1	1, 2, 3	Grand*/ Kji-qospem / Tlaqatik	18.8	45	303,068,120	369.2
2	4, 5, 6	Kinsac	1.7	18	8,757,768	116.0
3	7, 8	Third / Tqoskue'jk	0.9	24	7,066,280	10.3
4	9, 10	Second / Maqoqpejk	1.1	12	3,108,000	7.1
5	11	Powder Mill	0.4	13	1,787,424	26.6
6	12, 13	Rocky / Apjimoqikwitk	1.4	11	3,214,975	12.0
7	14, 15	Sandy	0.8	19	5,676,900	18.0
8	16	Paper Mill	0.2	6	367,290	33.7
9	17, 18	Kearney	0.6	26	5,658,920	27.7
10	19, 20	Susies Quarry**	1.3	10	4,210,000	13.6
11	21, 22	Governor	0.4	14	1,889,888	7.1
12	23, 24	Frasers	0.7	20	5,550,000	38.5
13	25	Bayers***	0.1	2.4	47,000	0.2
14	26	Second Chain	0.2	12	600,000	1.4
15	27	First Chain	0.2	12	850,000	2.2
16	28, 29, 30	Long	1.6	30	11,751,200	15.7
17	31	Williams / Etu'panuek	0.4	20	835,450	4.7
18	32	Colpitt†	0.2	12	1,243,683	2.3
19	33	Parr Governors††	0.5	unknown	unknown	21.0
20	34	Spruce Hill	1.0	12	3,342,200	4.1
21	35, 36, 37	Fletcher	1.0	11	2,575,741	141.4
22	38, 40	Thomas	1.1	15	4,100,000	126.0
23	40, 41, 42	William	3.0	28	27,025,000	74.2
24	43, 44, 45	Soldier	2.2	31	13,148,048	32.6
25	46, 47	Miller	1.3	13	3,874,923	43.1
26	48, 49	Spider	0.6	10	1,443,615	5.9
27	50, 51, 52, 53	Major	3.8	65	63,091,790	68.4
28	54, 55	Loon / Aneskewey Quspem	0.8	6	2,180,480	3.8
29	56, 57	Charles / A'se'pemk	1.4	28	10,383,040	20.8
30	58, 59	Micmac	1.0	6.1	2,953,600	22.1

Lake #	Sample #	Lake English Name / Lake Mi'kmaw Name	Surface Area (km^2)	~Max. Depth (m)	~Volume (m^3)	~Water-shed Area (km^2)
31	60, 61	Bissett	0.9	9	1,470,000	7.9
32	62, 63, 64	Morris / Loqutujk	1.6	13	3693150	18.6
33	65, 66	Russell	0.3	8	756,400	3.2
34	67	Frenchman	0.1	1.5	114,080	1.0
35	68	Anderson‡	0.6	26	4,812,600	5.0
36	69, 70	Banook / Panuk	0.4	12	862,470	24.3
37	71, 72	First / Asoqmasukwita'mk	0.8	23	4,332,501	3.4
38	73	Lemont	0.1	6	269,700	3.3
39	74	Topsail	0.6	7	1,542,993	2.2
40	75	Oathill	0.04	8.5	185,953	0.7
41	76	Penhorn	0.04	9	124,525	0.2
42	77	Maynard	0.1	15	351,025	0.2
43	78	Little Albro	0.03	4	60,000	1.1
44	79	Albro	0.2	6	359,450	0.9
45	80	Cranberry	0.1	3	182,211	0.9
46	81	Settle	0.05	7	125,718	0.3
47	82	Bell	0.1	8.5	253,270	0.3
48	83	Chocolate	0.1	13	273,075	3.0
49	84	Whimsical	0.02	unknown	unknown	0.4
50	85	Frog Pond	0.05	6	63,293	1.1
51	86	Power Pond‡	0.1	9	319,206	33.2
n/a	n/a	Ragged‡‡	n/a	n/a	n/a	n/a

*Official name is "Shubenacadie Grand Lake" but it is often locally referred to as "Grand Lake," which is also the name used in the previous reports.

**Susies Lake (sample 20) drains into Quarry Lake (sample 19). The two lakes were mistakenly treated as a single lake in previous surveys and were referred to as "Susies Lake" and the measurements from each sample were averaged. For consistency, measurements from the two lakes in 2021 were also averaged.

***Certain subsamples were lost in transit in 1991 and as such a number of parameters were unable to be measured.

†Official name is "Colpitt Lake" but was referred to as "Colbart Lake" in previous reports.

††Official name is "Governors Lake" but was referred to as "Parr Lake" in previous reports. Names were combined to prevent confusion with Governor Lake.

‡Not sampled in 1980.

‡‡Ragged Lake was only sampled in 1980 but accidentally omitted in 1991 and thus excluded from subsequent surveys.

Figure A.1. *Annual total precipitation from 1979 to 2021 with trendline (red), confidence interval (grey), trendline equation, R^2 value, and p-value.*

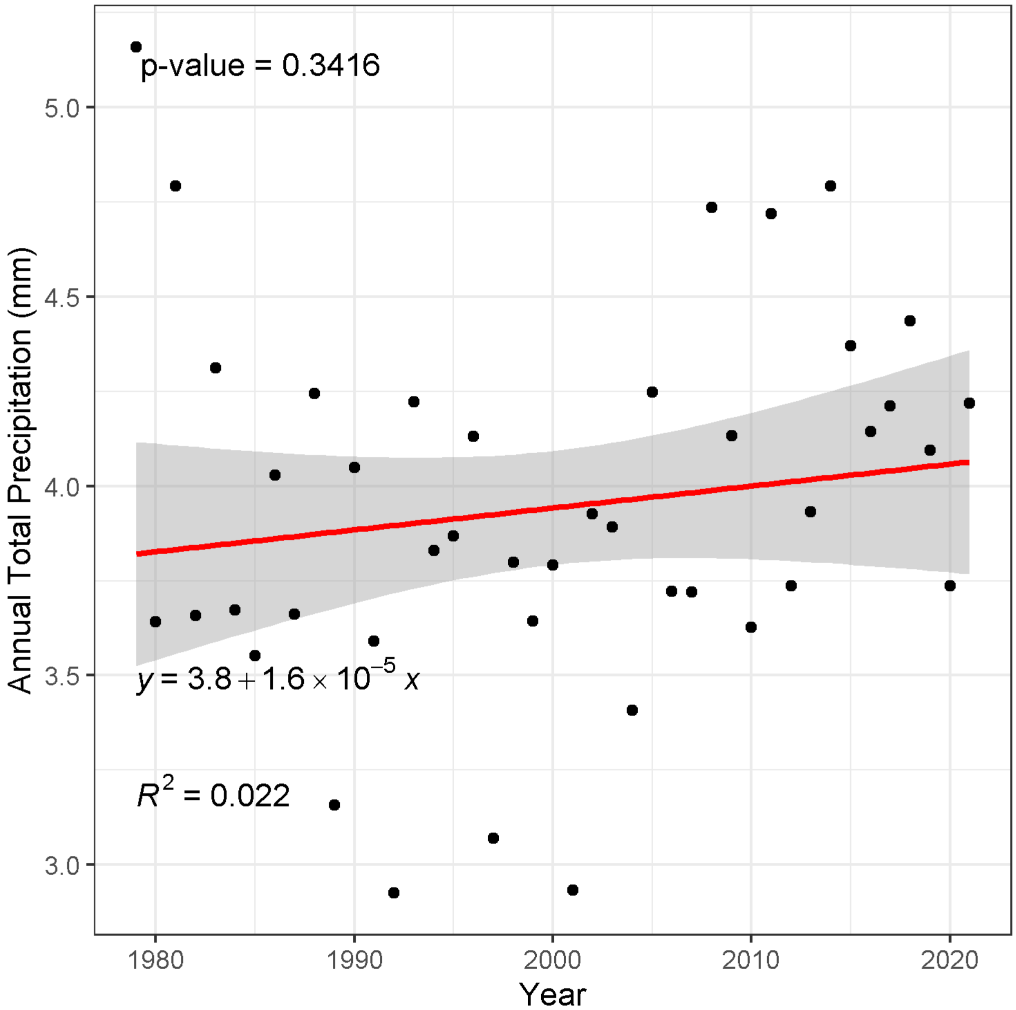


Table A.2. *Summary of five WWTF discharging (directly or indirectly) into study lakes. Study lakes are indicated in italics, including William, Thomas, Fletcher, Grand, Kinsac, Soldier, and Miller.*

Name	**Date Constructed**	**Treatment Process**	**Discharge (m^3/day)**	**Receiving System**	**Indirectly Affected Study Lakes**
Frame Subdivision (Waverly)	Early 1970	Tertiary	80	*William*	*Thomas, Fletcher, Grand*
Lockview-MacPherson (Fall River)	1994	Tertiary	455	Fletcher's Run	*Fletcher, Grand*
Wellington	Early 1970	Tertiary	68	*Grand*	
Springfield Lake	1987	Secondary	543	Lisle Lake	*Kinsac, Grand*
Aerotech Park	1986	Tertiary	1360	Johnson River System	*Soldier, Miller, Thomas, Fletcher, Grand*

Table A.3. *List of the 23 selected water quality parameters along with units of measurement and information regarding discrepancies and changes in analytical methods over time.*

Select Parameters:		**Units:**	**Notes**
1	Alkalinity	mg $CaCO_3$ / L	As a result of changes in analytical methods over the years, measurements were binned for among-year comparisons (trend analyses), but raw values were used for PCAs.
2	Aluminum (Al)	mg Al /L	1991 measurements deemed questionable (Clement et al. 2007; Clement and Gordon 2019).
3	Ammonia (NH_3)	mg N /L	1980 values deemed questionable and there is little confidence in perceived differences among years as ammonia is unstable and thus sensitive to slight differences in sample processing (Clement and Gordon 2019).
4	Arsenic (As)	µg As /L	1991 measurements deemed questionable (Clement et al. 2007; Clement and Gordon 2019).
5	Calcium (Ca)	mg Ca /L	
6	Chloride (Cl)	mg Cl /L	
7	Chlorophyll *a* (Chl *a*)	µg /L	Although new methods (Welschmeyer) of measuring Chl *a* have become common practice, the older acidification method was used for all years to be consistent. The results of both methods in 2021 were verified to be in high agreement.
8	Color	True Colour Units (TCU)	
9	Conductivity	µS/cm	Discrepancies between experimental and theoretical conductivity values from 1980 attributed to experimental conductivity measurement error by earlier reports (Clement et al. 2007; Clement and Gordon 2019), but the discrepancy could just as likely have resulted from error measuring the major cations and anions from which theoretical conductivity was calculated.
10	Copper (Cu)	µg Cu /L	1991 measurements deemed questionable (Clement et al. 2007; Clement and Gordon 2019).
11	Dissolved organic carbon (DOC)	mg C /L	Not measured in 1980. Measurement method in 1991 (wet oxidation) may have underestimated DOC content by as much as by as much as 20-40% (Koprivnjak et al. 1994). In 2000, total organic carbon (TOC) was measured instead of DOC but was believed to be comparable as little particulate carbon was observed (Clement et al. 2007).
12	Iron (Fe)	µg Fe /L	1991 measurements deemed questionable (Clement et al. 2007; Clement and Gordon 2019).

Select Parameters:		Units:	Notes
13	Magnesium (Mg)	mg Mg /L	
14	Manganese (Mn)	µg Mn /L	1991 measurements deemed questionable (Clement et al. 2007; Clement and Gordon 2019).
15	Nitrate (NO_3)	mg N /L	"Nitrate + nitrite" might have been measured in 1980 and 2000 rather than just nitrate, however nitrite likely contributed very little to these measurements based on the measured nitrite values in 2021, which were all below the detection limit.
16	pH	pH units, or [H^+]	Samples were measured immediately following collection in 1991 but the measurements were discarded due to a faulty probe and replaced with measurements taken several weeks after collection.
17	Potassium (K)	mg K /L	
18	Silica (Si)	mg Si /L	Measurements taken prior to 2021 are deemed unreliable due to differences in analytical methods in 1980 and the freezing of samples in 1991, 2000, and 2011, which can lead to underestimation of reactive silica (Lipps et al. 2018).
19	Sodium (Na)	mg Na /L	
20	Sulphate (SO_4)	mg SO_4 /L	1980 results were converted to match the units of each subsequent survey (mg S /L to mg SO_4/L).
21	Total nitrogen (TN)	mg N /L	2021 – One of the two samples collected from Miller, one of two samples from Charles, one of four samples collected from Micmac, and one of two samples collected from Sandy were found to be unusually high (not in high agreement with the replicate measurements or the nitrate and ammonia values measured at a different laboratory) and therefore are believed to be a result of procedural errors and have been removed.
22	Total phosphorus (TP)	mg P /L	Measurement from Frenchman in 1980 deemed a result of procedural error and discarded (Gordon et al. 1981). Replicate samples from Russell Lake in 1980 not in high agreement but the measurements were retained. Bissett Lake's measurement from 2011 was identified as an outlier and deemed to be a result of a typo and was corrected.
23	Zinc (Zn)	µg Zn /L	1991 measurements deemed questionable (Clement et al. 2007; Clement and Gordon 2019)

Table A.4. *List of data used for spatial analysis, along with their specific uses and sources.*

Data	Use
Cartographic boundary file of the Canadian provinces and territories (Statistics Canada 2016).	Creation of inset map for study area figure.
Cartographic boundary file for the United States of America (United States Census Bureau 2018).	Creation of inset map for study area figure.
Digital elevation model (DEM) at 20 m resolution for the province of Nova Scotia (NSDNRR 2006).	DEM for watershed delineation.
DEM at 5 m resolution for the HRM (HRMOD 2018).	DEM for watershed delineation.
Hydrographic network file for the province of Nova Scotia including linear, point, and polygon features (Province of Nova Scotia 2020).	Stream network for watershed delineation.
Landsat 4 TM image of HRM from 1982 (earliest available imagery during leaf-on period and with little cloud cover) (USGS 1982).	Land cover classification (1982).
Landsat 5 TM image of HRM from 1985 (USGS 1985).	Land cover classification to produce ~1980 mosaic.
Landsat 8 OLI image of HRM from 2020 (USGS 2020).	Land cover classification (2020).
Current (1992 – present) forest inventory for Halifax West and Hants County (NSDNRR 2021).	Amend land cover classifications; identify barrens and rock barrens.
Wetland vegetation and classification inventory for the province of Nova Scotia (NSDNRR n.d.).	Amend land cover classifications; identify wetlands.
Addressed road network for province of Nova Scotia (Province of Nova Scotia 2022a).	Paved road density analysis.

Table A.5. *a) Overall accuracy, kappa statistics, and confidence intervals for the mosaicked ~1980 classified image, and the 2020 classified image based on 500 randomly generated (stratified by class) points, b) Accuracy by informational class for the ~1980 mosaicked classification, c) Accuracy by informational class for the 2020 classification.*

a)

Thematic Output	Overall Accuracy	Lower 95% CI	Upper 95% CI	Kappa Statistic
~1980	0.968	0.9486	0.9816	0.915
2020	0.958	0.9365	0.9738	0.8999

b)

	Water	Developed	Undeveloped
Producer's Accuracy / Sensitivity	0.9857	0.8222	0.9818
User's Accuracy / Positive Predictive Value	0.9583	0.9024	0.9767
Balanced Accuracy	0.9894	0.9067	0.9518

c)

	Water	Developed	Undeveloped
Producer's Accuracy / Sensitivity	0.9571	0.8525	0.9756
User's Accuracy / Positive Predictive Value	0.9437	0.8814	0.973
Balanced Accuracy	0.9739	0.9183	0.9496

Figure A.2. a) – v) *Electronic Supplement 1 is available in PDF format at DalSpace. It contains 22 subplots (boxplots with Kruskal Wallis results), labelled a) – v), evaluating collective differences among years in 22 water quality parameters.*

Figure A.3. a) – u) *Electronic Supplement 2 is available in PDF format at DalSpace. It contains 21 subplots (simple linear regression line plots), labelled a) – u), evaluating linear trends in 21 water quality parameters within each of the study lakes.*

Figure A.4. *Pair plots revealing multicollinearity among explanatory variables with data distribution histograms along the diagonal.*

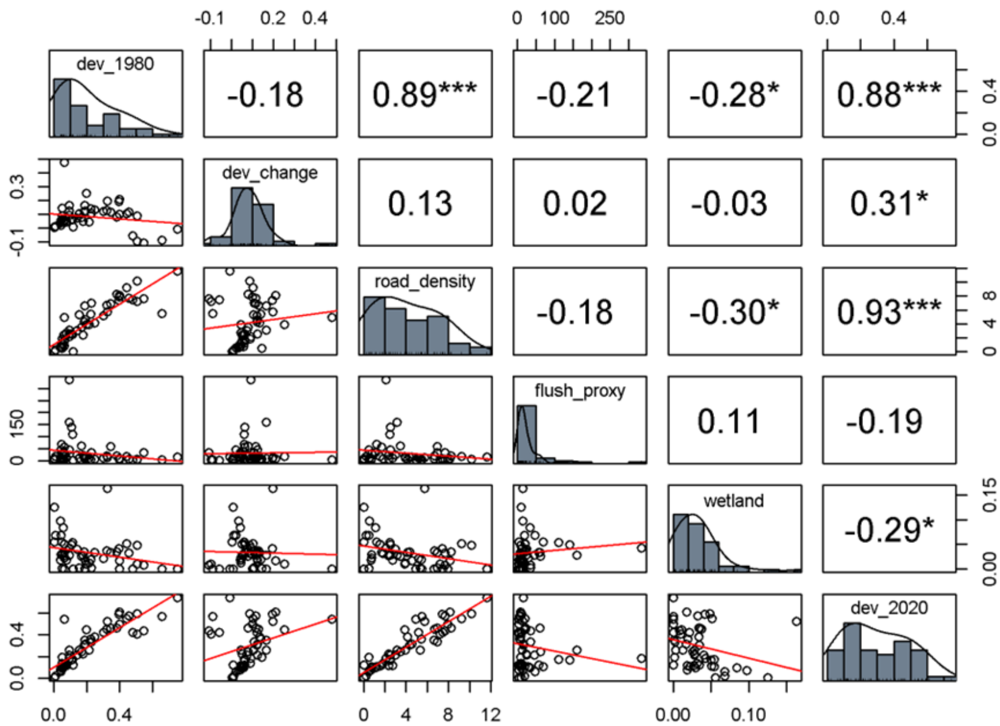


Table A.6. *a) Full linear regression equations with intercept and coefficient significance indicated, where p < 0.05 (*), p < 0.01 (**), p < 0.001 (***), and p < 0.0001 (****), b) Assumptions tests results for each of the regression models. P-values indicating a violation of the assumptions are in bold.*

a)

Model	**Response Variable**	**Equation**
a)	ΔChloride	= 190.93(dev_1980)*** + 290.95(dev_change)** – 24.62
b)	ΔCalcium	= 24.175(dev_change)** + 2.105.
c)	ΔColor	= 0.113(flush_proxy)** – 27.132(dev_1980)** + 9.598**
d)	ΔDOC	= 0.008(flush_proxy)* + 12.718(wetland)* + 1.752**
e)	ΔMagnesium	= 4.161(dev_change)*** – 0.032
f)	ΔSulphate	= 42.003(dev_change)** – 5.597**
g)	ΔTP	= 0.018(dev_1980)** – 0.001

b)

Model	**Independence** *Durbin-Watson Test*	**Linearity** *RESET Test*	**Residual Homoscedasticity** *Breusch-Pagan Test*	**Residual Normality** *Shapiro-Wilks*
a)	p = 0.3575	p = 0.217	p = 0.1666	**p = 2.82e-08**
b)	**p = 0.0245**	p = 0.1283	p = 0.6435	**p = 4.876e-07**
c)	p = 0.09234	p = 0.08977	p = 0.2665	**p = 0.0006052**
d)	**p = 0.04712**	p = 0.2107	p = 0.2962	p = 0.1433
e)	p = 0.4956	p = 0.1662	p = 0.2765	**p = 3.144e-05**
f)	**p = 0.03732**	p = 0.5912	p = 0.2044	**p = 2.249e-06**
g)	p = 0.6388	p = 0.4104	p = 0.3783	**p = 2.27e-05**

Figure A.5. *Scree plot for PCA of scaled 2021 data.*

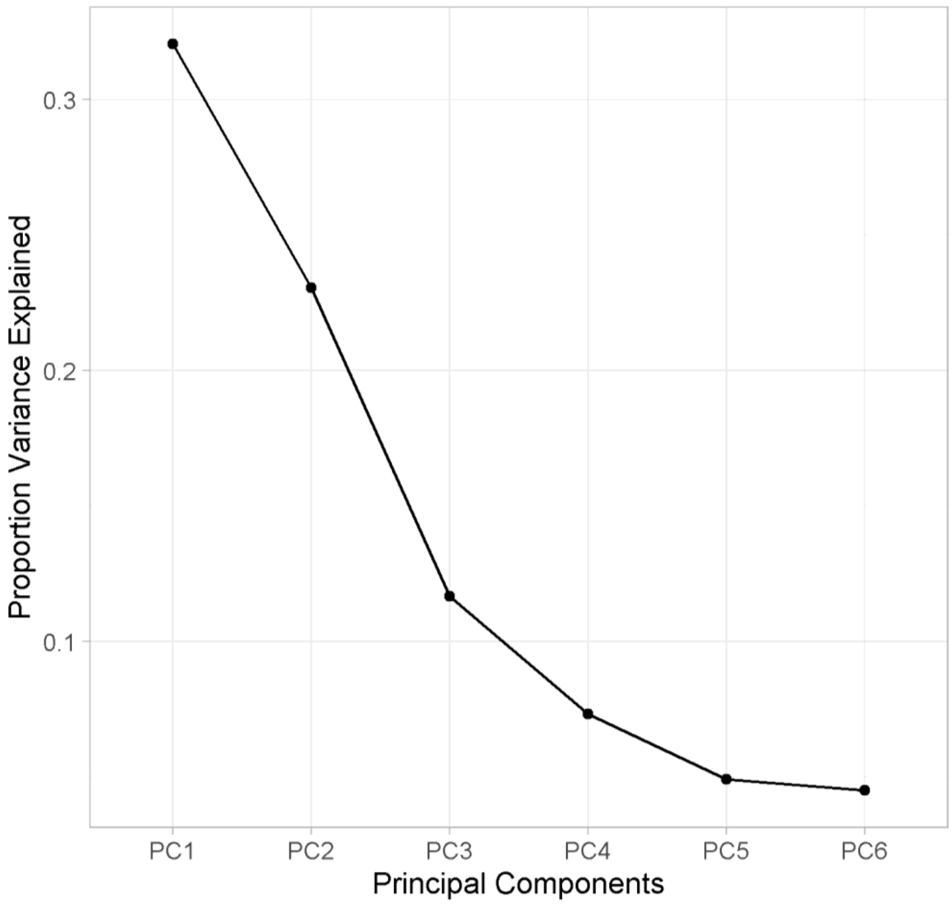


Table A.7. *Loadings for Principal Components (PC) 1, 2, and 3, together accounting for 67% of the variability in the data. Loadings greater than 0.3 are bolded.*

	PC1 Major Ions	**PC2** Trace Elements & pH	**PC3** Nutrients & Colour
Conductivity	**0.333**	-0.035	0.050
Calcium	**0.325**	-0.063	0.031
Potassium	**0.314**	-0.076	0.100
Sodium	**0.311**	-0.054	0.047
Magnesium	**0.310**	0.207	0.096
Chloride	**0.306**	-0.056	0.035
Alkalinity	0.272	-0.228	-0.010
Sulphate	0.223	**0.326**	0.025
Copper	0.191	0.167	0.115
pH	0.187	**-0.334**	0.028
Manganese	0.150	**0.378**	0.016
TP	0.126	-0.17	**0.367**
Zinc	0.103	**0.407**	0.031
Nitrate	0.099	-0.052	**0.395**
Chlorophyll *a*	0.082	-0.188	-0.009
Arsenic	0.063	-0.085	0.072
Aluminum	0.043	**0.382**	0.011
TN	0.027	-0.130	**0.365**
Ammonia	0.026	-0.027	-0.092
Silica	-0.120	0.265	0.294
Iron	-0.127	0.112	**0.438**
Color	-0.213	-0.007	**0.353**
DOC	-0.233	-0.114	**0.342**

Table A.8. *United States Environmental Protection Agency (US EPA) Categorization for Freshwater Alkalinity Levels (Godfrey et al. 1996).*

US EPA Category	Concentration $CaCO_3$ (mg/L)
Acidified	< 1
Critical	< 2
Endangered	2 - 5
Highly Sensitive	5 - 10
Sensitive	10 - 20
Not Sensitive	> 20

Figure A.6. *Shift in alkalinity since 1980 in study lakes presented as the percentage belonging to each alkalinity category based on the US EPA categorization scheme (Table A.8), where < 5mg $CaCO_3$/L is considered Endangered, Critical, or Acidified, 5 - 10 mg $CaCO_3$/L is Highly Sensitive, 10 – 20 mg $CaCO_3$/L is Sensitive, and > 20 mg $CaCO_3$/L is deemed Not Sensitive.*

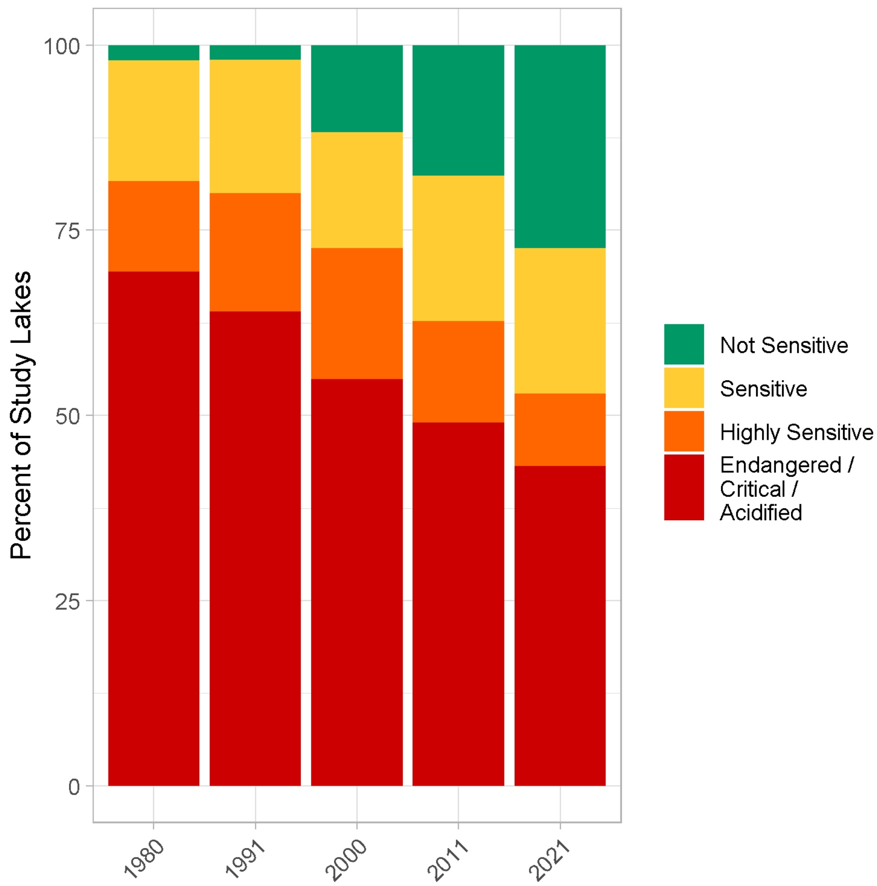
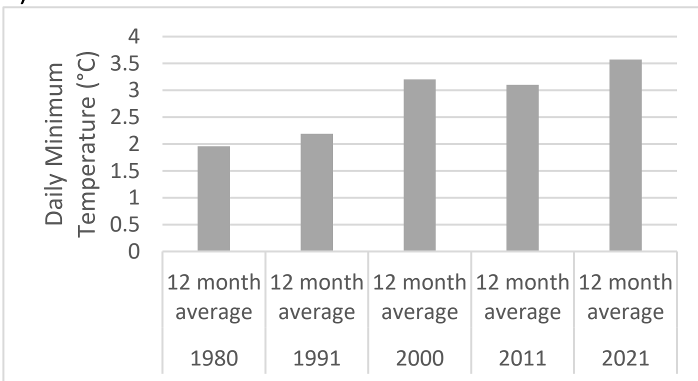
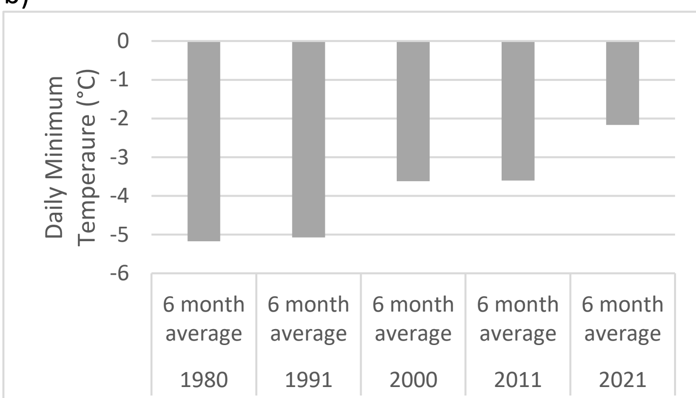


Figure A.7. *Mean daily-minimum temperatures calculated for the a) 12- and b) 6-month periods prior to each synoptic survey, as well as c) total precipitation (mm) calculated for the 12- and 6-month periods prior to each synoptic survey.*

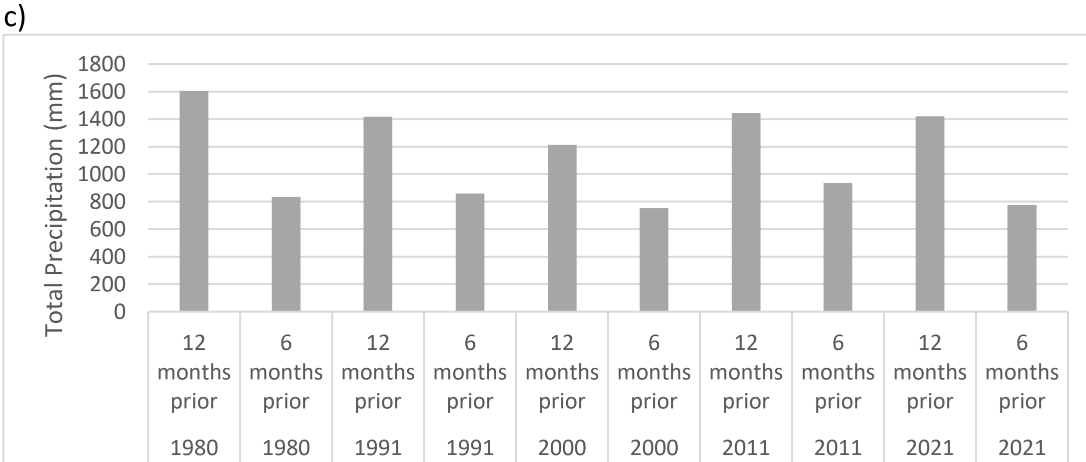
a)



b)



c)



APPENDIX B – CHAPTER 3 SUPPLEMENTARY MATERIALS

Table B.1. *Canadian Council of Ministers of the Environment (2004) trophic trigger ranges based on total phosphorus (TP) concentration for freshwaters.*

Trophic Status	Canadian Trigger Ranges Total Phosphorus (µg/L)
Ultra-oligotrophic	< 4
Oligotrophic	4 – 10
Mesotrophic	10 – 20
Meso-eutrophic	20 – 35
Eutrophic	35 – 100
Hyper-eutrophic	> 100

Table B.2. *List of data used in the study area map and their sources.*

Feature	Data source
Inset map	Cartographic boundary file of the Canadian provinces and territories (Statistics Canada 2016).
Inset map	Cartographic boundary file for the United States of America (United States Census Bureau 2018).
Waterbodies	Hydrographic network file for the province of Nova Scotia including linear, point, and polygon features (Province of Nova Scotia 2020).
Roads	Addressed road network for province of Nova Scotia (Province of Nova Scotia 2022a).

Figure B.1. *Electronic Supplement 3 is available in PDF format at DalSpace. It contains fourteen plots (one for each of the Synoptic Water Quality Study lake basins), each comprised of three depth profiles plotted on a common depth axis (30 m) to show relative depth of each basin: one depicting temperature (°C; red), one depicting dissolved oxygen (DO; mg/L; blue), and one depicting total phosphorus (TP; µg/L; green) from the August sampling session (peak stratification).*

Table B.3. *Anoxic layer statistics from peak stratification (August) sampling session.*

Lake/basin	Upper sample depth (m)	Upper DO conc. (mg/L)	Lower sample depth (m)	Lower DO conc. (mg/L)	Max. depth (m)	Anoxic layer thickness (m)	% of water column anoxic
Bissett	5.0	0.75	9.0	0.07	10	5	50
Colpitt	7.0	0.99	10.5	0.29	12	5	42
Susies	5.5	0.82	10.0	0.47	10	4.5	45
Penhorn	5.0	0.31	8.5	0.21	9	4	44
Fletcher	8.0	0.10	9.5	0.05	11	3	27
Sandy 1	18	0.62	18.5	0.47	21	3	14
Frasers	18	0.65	19.5	0.14	20	2	10
Charles 2	13	0.60	14.4	0.10	14	1	7

Table B.4. *List of deviations from methodology organized by the sampling session during which they occurred and the lake basin they apply to.*

Session	Lake(s)	Deviation Explanation
1	Charles 1, Charles 2, Sandy 1, Sandy 2	Chl *a* and TP samples were only collected from the surface, middle, and bottom of the lake basin water columns.
2	Albro	High discrepancy was observed between the Chl *a* concentration measured in duplicates of the sample collected at a depth of 3 m so a third replicate was run and confirmed that the presence of a large quantity of particulate matter was responsible for the observed heterogeneity.
2	Frasers, Spider, Fish	Welschmeyer-derived Chl *a* results were inexplicably high and were thus substituted with the results obtained through the acidification method. The acidification results were deemed accurate as they were similar to concentrations measured during the previous and later sampling session. Generally, the results derived from the Welschmeyer method and the acidification method were in high agreement and as such, the acidification results were deemed a suitable substitute.
3	Bissett	TP sample collected at 9 m (sample closest to the bottom) had to be discarded due to contamination with sediment and was thus excluded from all TP metric calculations.
3	Spider, Fish	Due to equipment failure, the Welschmeyer-derived Chl *a* results were compromised and as such were substituted with the acidification results.
3	Most lakes	Due to equipment failure, TP samples were not measured within 24 hours but were instead frozen at -20°C for a period of several weeks before being thawed and measured.
3	Anderson, Bissett, Charles 1, Charles 2, Fletcher, Penhorn, Sandy 1, Sandy 2	Chl *a* samples were not measured immediately and instead remained in the refrigerator for a period of 2 weeks but the samples were deemed to not be degraded.
4	Penhorn	Fall overturn incomplete; lake remained stratified when sampled on October 14, 2021. Results were excluded from all analyses and Penhorn was resampled on December 1, 2021, at which point it was no longer stratified.
4	Anderson, Colpitt, Spider, Susies, Bissett*	Fall overturn incomplete; lakes remained stratified. *Bissett Lake was not thermally stratified but dissolved oxygen and TP concentrations remained strongly stratified.
4	Sandy 1, Sandy 2	Sampling occurred following a large rainfall event that could have influenced measurements.