

**Using Integrated Environmental Change Study Methods to Understand Factors  
Influencing Harmful Algae Blooms in a Rural Headwater Lake**

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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# Table of Contents

List of Tables .....	v
List of Figures .....	vi
Abstract .....	viii
List of Abbreviations and Symbols Used .....	ix
Acknowledgements .....	xi
Chapter 1 Introduction .....	1
1.1 Context .....	1
1.2 Study Area .....	4
1.3 Thesis Objectives .....	6
Chapter 2 Literature Review .....	8
2.1 Lake Characterization .....	8
2.1.1 Trophic State .....	8
2.1.2 Thermal Mixing Regime .....	10
2.2 Climate Change and Lakes .....	11
2.2.1 Physical Impacts .....	11
2.2.2 Chemical Impacts .....	11
2.2.3 Biological Impacts .....	13
2.3 Trophic State Deviation .....	14
2.3.1 Risk Factors .....	14
2.3.2 Internal Phosphorus Loading .....	15
2.4 Applied Paleolimnological Assessment .....	18
2.4.1 Radiometric Dating .....	18
2.4.2 Productivity .....	18
2.4.3 Geochemistry .....	19

2.4.4	Linkage with Climate Records.....	21
Chapter 3	Methodology.....	23
3.1	Climate Data Retrieval and Analysis .....	23
3.2	Lake Water Sampling.....	24
3.2.1	Lake Morphometry .....	24
3.2.2	Water Quality Monitoring.....	25
3.2.3	In-situ Measurements.....	27
3.3	Landscape Change.....	30
3.3.1	Landsat Imagery Collection.....	30
3.3.2	Landcover Change Digitization .....	30
3.3.3	Application of Normalized Difference Vegetation Index.....	30
3.3.4	Uncertainty.....	31
3.4	Sediment Sampling .....	32
3.5	Sediment Analysis.....	32
3.5.1	<sup>210</sup> Pb Dating .....	32
3.5.2	Total Metals .....	33
3.5.3	Chlorophyll-a .....	33
3.5.4	Statistical Methods.....	34
Chapter 4	Results and Discussion.....	36
4.1	Weather and Climate.....	36
4.1.1	Air Temperature.....	36
4.1.2	Total Annual Precipitation.....	39
4.2	Lake Characteristics .....	40
4.2.1	Morphometry .....	40
4.2.2	General Water Chemistry .....	41

4.2.3	Trophic status.....	42
4.2.4	In situ Water Chemistry Profiles.....	45
4.3	Landscape change .....	55
4.3.1	Road and Residential Infrastructure Development.....	55
4.3.2	Forest Removal Activities.....	56
4.4	Sediment Bulk Biogeochemistry.....	64
4.4.1	Radiometric Dating.....	64
4.4.2	Biogeochemistry Profiles.....	65
4.4.3	Principal Component Analysis .....	71
4.4.4	General Linear Model.....	73
4.5	Synopsis of Results and Discussion.....	76
Chapter 5	Conclusion.....	81
5.1.1	Recommendations for Management of Mattatall Lake .....	82
5.1.2	Lessons for Lake Managers and Researchers .....	83
5.1.3	Future Research .....	84
References	.....	85
APPENDIX A – SUPPLIMENTAL FIGURES	.....	99

## List of Tables

TABLE 2.1: SUMMARY OF TROPHIC STATE THRESHOLD LIMITS. TP LIMITS ARE FROM CCME (2004). CHLOROPHYLL-A AND SECCHI DEPTH LIMITS ARE FROM VOLLENWEIDER AND KEREKES (1982). .....	10
TABLE 3.1: SELECTED ECCC WEATHER STATIONS, THEIR RELATIVE DISTANCES FROM WENTWORTH, NS, AND DURATION OF RECORD.....	23
TABLE 3.2: METADATA OF LANDSAT IMAGES USED. ....	30
TABLE 4.1: LAKE MORPHOLOGICAL CHARACTERISTICS .....	40
TABLE 4.2: SUMMARY OF WATER QUALITY PARAMETERS AND THEIR REPORTING DETECTION LIMITS (RDL) MEASURED IN MATTATALL LAKE AND ANGEVINE LAKE. ....	43
TABLE 4.3: PARAMETER VALUES FOR TROPHIC STATE EVALUATION FOR MATTATALL LAKE AND ANGEVINE LAKE. MEAN VALUES ARE PRESENTED AS THE MEAN ± STANDARD DEVIATION....	44
TABLE 4.4: TROPHIC STATE CLASSIFICATION OF MATTATALL AND ANGEVINE LAKES, WHERE M = MESOTROPHIC AND O = OLIGOTROPHIC.....	44
TABLE 4.5: LAND USE TYPES FOR THE MATTATALL LAKE WATERSHED IN 1985 VERSUS 2016 FROM CWRS (2017). LAND USE CATEGORIES TOTALS ARE EXPRESSED AS A VALUE FOLLOWED BY THE PERCENT COVER IN PARENTHESES.....	56
TABLE 4.6: APPROXIMATE AREAS OF DEFORESTATION DETECTED FROM LANDSAT IMAGERY IN THE MATTATALL LAKE WATERSHED. AREAS WERE CONVERTED FROM 30 × 30 M CELL COUNTS TO HECTARES (HA).....	61
TABLE 4.7: APPROXIMATE AREAS OF DEFORESTATION DETECTED FROM LANDSAT IMAGERY IN THE ANGEVINE LAKE WATERSHED. AREAS WERE CONVERTED FROM 30 × 30 M CELL COUNTS TO HECTARES (HA).....	61
TABLE 4.8: GLM MODEL VARIATIONS AND TESTS .....	75
TABLE 4.9: ASSUMPTION TEST RESULTS AND INTERPRETATIONS FOR THE M4 MODEL. ....	75
TABLE 4.10: SUMMARY OF VARIABLE COEFFICIENTS, ERROR AND SIGNIFICANCE FOR MODEL M4 . ....	75

## List of Figures

FIGURE 1.1: MAP OF THE STUDY AREA INCLUDING MATTATALL AND ANGEVINE LAKES AND THEIR RESPECTIVE WATERSHED BOUNDARIES. ....	6
FIGURE 3.1: SAMPLING LOCATIONS AND BATHYMETRY OF MATTATALL LAKE. WATER QUALITY SAMPLING AND IN-SITU MEASUREMENTS WERE TAKEN AT BASIN 1, 2 AND 3. A GRAVITY CORE WAS COLLECTED AT BASIN 1. WATER DEPTH CONTOURS ARE SHOWN AT 1 M INTERVALS.....	28
FIGURE 3.2: SAMPLE LOCATION AND BATHYMETRY OF ANGEVINE LAKE. WATER QUALITY SAMPLING, IN-SITU MEASUREMENTS, AND GRAVITY CORE COLLECTION ALL OCCURRED WITHIN THE CENTRAL BASIN. WATER DEPTH CONTOURS ARE SHOWN AT 1 M INTERVALS. ....	29
FIGURE 4.1: AVERAGE MINIMUM AIR TEMPERATURES FOR ANNUAL (A), SUMMER (B) AND FALL (C) FROM 1873 TO 2019. BLUE REGRESSION LINES ARE ACCOMPANIED BY A 95% CI IN GREY. A LOESS CURVE WITH A SPAN OF 0.15 IS SHOWN IN BLACK. EACH PLOT IS LABELLED WITH THE OVERALL CHANGE IN AIR TEMPERATURE FOR THAT PLOT. ....	38
FIGURE 4.2 TOTAL ANNUAL PRECIPITATION FROM 1873 TO 2019. A BLUE REGRESSION LINE IS ACCOMPANIED BY A 95% CI IN GREY, THIS LINE WAS NOT SIGNIFICANT. A LOESS CURVE WITH A SPAN OF 0.15 IS SHOWN IN BLACK. ....	39
FIGURE 4.3: WATER TEMPERATURE PROFILES FOR MATTATALL AND ANGEVINE LAKES. ....	46
FIGURE 4.4: DISSOLVED OXYGEN PROFILES FOR MATTATALL AND ANGEVINE LAKES. ....	47
FIGURE 4.5: TOTAL PHOSPHORUS PROFILES FOR MATTATALL AND ANGEVINE LAKES.....	50
FIGURE 4.6: SOLUBLE REACTIVE PHOSPHORUS PROFILES FOR MATTATALL AND ANGEVINE LAKES.....	51
FIGURE 4.7: CHLOROPHYLL-A PROFILES IN MATTATALL AND ANGEVINE LAKES. ....	54
FIGURE 4.8: AREAS OF DEFORESTATION IN THE MATTATALL LAKE AND ANGEVINE LAKE WATERSHEDS FROM 1985 TO 2018. DELINEATED FROM USGS LANDSAT IMAGERY.....	58
FIGURE 4.9: COMPOSITE BAND IMAGES OF MATTATALL AND ANGEVINE LAKE WATERSHEDS, WHERE BAND_2 IS THE FIRST (EARLIER) STUDY IMAGE, AND BAND_1 IS THE SECOND (LATER) STUDY IMAGE. ....	59
FIGURE 4.10: CONTINUATION OF COMPOSITE BAND IMAGES OF MATTATALL AND ANGEVINE LAKE WATERSHEDS, WHERE BAND_2 IS THE FIRST (EARLIER) STUDY IMAGE, AND BAND_1 IS THE SECOND (LATER) STUDY IMAGE. ....	60
FIGURE 4.11: ESTIMATED CRS <sup>120</sup> Pb DATE VERSUS CORE DEPTH FOR MATTATALL AND ANGEVINE LAKES. ....	64

FIGURE 4.12: SPECTRALLY INFERRED SEDIMENT CHL-A AND TOTAL METALS PROFILES FOR MATTATALL AND ANGEVINE LAKES. ELEMENTS FOLLOWED BY (%) ARE THE CONCENTRATION IN PPM DIVIDED BY 10000. .... 66

FIGURE 4.13: RATIO OF MN/FE IN MATTATALL AND ANGEVINE LAKES. THE TOP 5 CM WAS REMOVED FROM BOTH GRAPHS TO SIMPLIFY INTERPRETATION. .... 70

FIGURE 4.14: PCA BIPLLOT OF THE MATTATALL AND ANGEVINE LAKES SEDIMENT PROXIES. 50-YEAR INTERVALS UNTIL PRE-1870 ARE DENOTED BY COLOUR INTENSITY. .... 72

FIGURE 4.15: PAIR PLOTS OF THE PARAMETERS OF INTEREST ARE SHOWN IN THE TOP RIGHT OF THE PLOT. CORRESPONDING R VALUES ARE REPORTED IN THE BOTTOM LEFT OF THE PLOT.... 73

## **Abstract**

Eutrophication and algae production are an important lake management issue in rural Nova Scotia. In the past decade, there have been increasing instances of harmful algae bloom (HAB) events in previously unaffected surface water systems. Three major toxic cyanobacteria bloom events of *Dolichospermum planctonicum* were observed in Mattatall Lake in Cumberland County in 2014, 2015 and 2016. The bloom events were considered unprecedented for Mattatall Lake because it is a rural headwater lake where this level of productivity had not been observed before. This project utilized a multifaceted approach to studying the environmental changes at Mattatall Lake to parse what factors, cumulative or recent, might have contributed to the HAB events. A multiproxy paleolimnological assessment, in combination with historic climate and land use analysis, water quality monitoring, and comparison to a nearby reference site with no history of algae blooms was applied. Through a weight of evidence approach it was found that Mattatall Lake has natural attributes that predisposed the lake to HAB vulnerability. These include the unique morphometry of the lake and how this influenced its ability support primary producers. When these vulnerabilities are superimposed by watershed destabilization and climate change, the risk of HABs occurring is amplified because the threshold for cyanobacteria habitability in Mattatall Lake is lowered.



## List of Abbreviations and Symbols Used

%	Percent
°C	Degrees Celsius
µg	Micrograms
µm	Micrometre
µS	Microsiemens
AIC	Akeike information criterion
A <sub>l</sub>	Area of lake
A <sub>ws</sub>	Area of watershed
BV	Bureau Veritas
CCME	Canadian Council of Ministers of the Environment
chl-a	Chlorophyll-a
cm	Centimetre
CRM	Certified reference material
CRS	Constant rate of supply
CWRS	Centre for Water Resources Studies
DEM	Digital elevation model
DO	Dissolved oxygen
DOC	Dissolved organic carbon
dv	DownVu
E	Evaporation
ECCC	Environment and Climate Change Canada
GLM	General linear model
ha	Hectare
HAB(s)	Harmful algae bloom(s)
hrs	Hours
Hz	Hertz
IPCC	Intergovernmental Panel on Climate Change
L	Litre
m	Metre

mg	Milligram
mL	Millilitre
NAO	North Atlantic Oscillation
NDVI	Normalized difference vegetation index
NIR	Near infrared light
NS	Nova Scotia
OECD	Organization for Economic Co-operation and Development
PC	Principal component
PCA	Principal components analysis
PEARL	Paleoecological Environmental Assessment and Research Laboratory
ppm	Parts per million
$P_r$	Average annual precipitation
PVC	Polyvinyl chloride
Q	Outflow
R	Visible red light
RC	Average runoff coefficient
SD	Secchi depth
SRP	Soluble reactive phosphorus
TCU	Total colour units
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
USA	United States of America
USGS	United States Geological Survey
V	Volume
VRS	Visible ray spectroscopy
XRF	X-ray fluorescence
yr	Year

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# Chapter 1 Introduction

## 1.1 Context

Freshwater are typically managed with the goal to either maintain the current environmental state, or, to alter the ecosystem to a more desirable state. In either case it is important to understand the range of natural variability for the system to provide context and guidance for management (Landres et al., 1999). The main approaches to studying environmental change in lacustrine environments include: (1) monitoring, (2) space for time substitution, (3) modelling, and (4) paleoenvironmental data (Smol, 2008).

Monitoring in lakes typically involves sampling and testing for common water quality parameters of interest (temperature, pH, nutrients etc). Long term monitoring (repeated sampling over months or years) in the context of Nova Scotia (NS) lakes is limited, and non-existent for most lakes in rural areas (Johnston et al., 2021). In addition, monitoring data rarely have the duration and resolution to adequately account for natural variability (Smol, 2008). Space for time substitution utilizes a reference lake with similar characteristics to the study lake to represent past conditions. This is useful in the context of decoupling geogenic inputs from anthropogenic when there is a clear pollution source (e.g. Davidson et al., 2021). This method is weakened by assumptions that the lakes were similar in the past and respond similarly to natural and anthropogenic stressors.

Mathematical modelling to hindcast past environmental conditions and predict future conditions is a popular tool for environmental managers. Models are based on current conditions and processes, can utilize limited monitoring data, and can be optimized and validated to present conditions. Models have been used in NS to predict phosphorus (P) loading from watersheds based on watershed characteristics, and validated against contemporary lake water sample data (Brylinsky, 2004; Johnston et al., 2021). This approach has been effective in predicting lake trophic states, but predictions lack precision and do not account for past natural variability.

Paleoenvironmental data can be gathered from numerous environments in a variety of ways, but the commonality among them is sampling of relatively undisturbed consistent accumulation of matter (i.e. glaciers, ocean sediment basins, lake sediment basins, sedimentary rock units, peat bog accumulations etc.). The field of paleolimnology refers specifically to the study of lake

sediment basins. Paleoenvironmental data is a powerful tool that can be used in combination with the other environmental change study methods to resolve knowledge gaps of past environmental change, account for lacking monitoring data and evaluate model efficacy against actual historic data (Smol, 2008). Lake sediments are an integration of physical, chemical, and biological matter sourced from the lake pelagic and littoral zones and surrounding catchment drainage area. As sediments accumulate in lake basins, they are continually covered by succeeding layers (von Gunten et al., 1997). The character of these sediments is preserved as interaction with the overlying waterbody becomes limited in older layers as newer layers are added. Through extraction of sediment cores and analysis of proxy data, the record of past environmental change can be reconstructed at a resolution where natural variability can be observed (Smol, 1992).

Paleolimnology as an academic discipline has a long history, utilized first by geologists studying the lithified deposits of ancient lakes (Binford et al., 1983). In the mid-1900s ‘historical ecologists’ began to apply the same processes and concepts used in stratigraphy to the unconsolidated accumulations underlying modern lakes (Binford et al., 1983). Early paleolimnology studies focused on the ontogeny of lakes and used biological proxies such as diatoms and pollen that could be simply measured in both the water column and the lake sediments (Deevey, 1955; Walker, 1987). Geochemical methods arose in the 1960s as methods for extracting and analyzing elements in soils and sediments became available (Mackereth & Cooper, 1966). In the 1980s/90s focus began to shift to investigating human impacts. Diatom microfossils were used to study cultural eutrophication (Warwick, 1980) and acid rain (Battarbee et al., 1984) impacts on lakes. In more recent decades though, continued analytical and research advances in paleolimnology and adjacent environmental science fields has led to a proliferation of possible parameters and how they can be interpreted. Possible indicators outside the initial ecological focus of paleolimnology now include mineralogical (Last, 2001), inorganic geochemical (ex. elemental analysis, organic and inorganic carbon fractionation; Boyle, 2001), organic geochemical (ex. total organic carbon, total carbon/total nitrogen ratios, carbon/nitrogen stable isotopes, lignin oxidation products; Meyers & Teranes, 2001), and sedimentary pigment analysis (ex. chlorophylls and carotenoids; Leavitt & Hodgson, 2001). Modern paleolimnology studies aim to utilize multiple proxies from each sediment core which are carefully selected to inform investigators about specific conditions they are trying to better understand. It has been

suggested that the most defensible studies use geochemical analysis as a complement to biological indicators rather than using geochemistry independently (Boyle, 2001). This is because geochemical indicators can be influenced by overlying water chemistry, redox reactivity, and migration through the sediment post-deposition (Boyle, 2001).

Studies using biological proxies in combination with chemical and physical indicators have been demonstrated to be extremely informative. For example a paleolimnological study surveying several lakes in the Athabasca oil sands region of Alberta, Canada, demonstrated how these lakes have completely shifted in ecological state (Kurek et al., 2013). The study used a combination of proxies including polycyclic aromatic hydrocarbons, fossil pigments and paleoecological assessment of Cladoceran assemblages. Authors were able to establish critical information on baseline conditions in the study lakes and how oil sand development has impacted their function and ecology (Kurek et al., 2013).

These multiproxy paleolimnological studies tend to be undertaken independently by specialized labs because the techniques are labour intensive and time consuming. This can often conflict with short monitoring and management timelines in industry (Landres et al., 1999). As such, paleoenvironmental data does not often appear in consulting or government reports (Dunnington, 2015). These industries rather rely on the other three methods (space for time, monitoring and modelling) which can be rapidly and cost-effectively implemented in a short timeline. Use of paleolimnology is also limited in application by the supply of those with the expertise to accomplish such studies. In depth knowledge of taxonomy and life histories of the biological proxies is essential, and this knowledge base is not readily accessible or transferrable to those most often charged with lake management responsibilities (i.e. government, consulting firms, stewardship associations). This creates a bottleneck where there is an abundance of lakes with issues that could be better managed if paleoenvironmental data were available, but relatively few labs with the resources to undertake a comprehensive paleolimnological investigation.

There has been an ever-rising need to use wholistic approaches to understanding human impacts on valuable and limited freshwater resources, as anthropogenic climate change and pollution has continued to increase with rising human population. Partnership between academic paleolimnological investigators and lake managers is imperative to effectively respond to these

needs. As previously asserted, though, the time-consuming nature of paleolimnology studies and limited taxonomic expertise can be factors preventing traditional paleolimnology from being a practical component of studies conducted by government and consulting agencies. However, rapid proxy analysis techniques that are more accessible have been continually growing in their defensibility and transmissibility (elemental analysis, fossil pigments, stable isotopes etc). These rapid analysis methods have their own deficiencies and reducing the number of proxies coming from a given lake sediment core may increase risk of false assumptions. However, this thesis will argue that such methods could be utilized in combination with other environmental change study methods already being employed by applied scientists and consulting agencies (i.e. modelling, monitoring, reference sites), and thus attenuating the risk of misinterpretation. Combining even limited sediment core data with other lines of evidence strengthens the collective by:

- Improving the defensibility of estimated natural variability in study parameters,
- Providing pre-disturbance targets for remediation goals that are relevant to the region and/or lake body,
- Validating models such that they are not right for the wrong reasons,
- Improving and supporting management recommendations with evidence, and,
- Providing perspective on lake response/recovery to past historical events.

An integrated approach to lake study using rapid and applied paleolimnology techniques, contemporary water quality monitoring data, watershed modeling and reference site comparison will be implemented through the course of this study.

## 1.2 Study Area

This study is focused on identifying the processes contributing to harmful algae blooms (HABs) in Mattatall Lake; a rural headwater lake on the border of Cumberland and Colchester counties in Nova Scotia, Canada (Figure 1.1). HABs were observed in Mattatall Lake in the fall of 2014 and 2015, and the summer of 2016 (Nguyen-Quang et al., 2016). Anecdotally, the HABs in 2014 and 2015 occurred in the last two weeks of September. The 2014 HAB dissipated before the lake froze, while the 2015 bloom persisted and the lake surface froze while algae were still present. The HAB in 2016 occurred in the first week of August. The dominant bloom species for all three HAB events was identified as *Dolichospermum planctonicum* (Nguyen-Quang et al., 2016), formerly known as *Anabaena planctonica* (Kelly et al., 2021). This species of

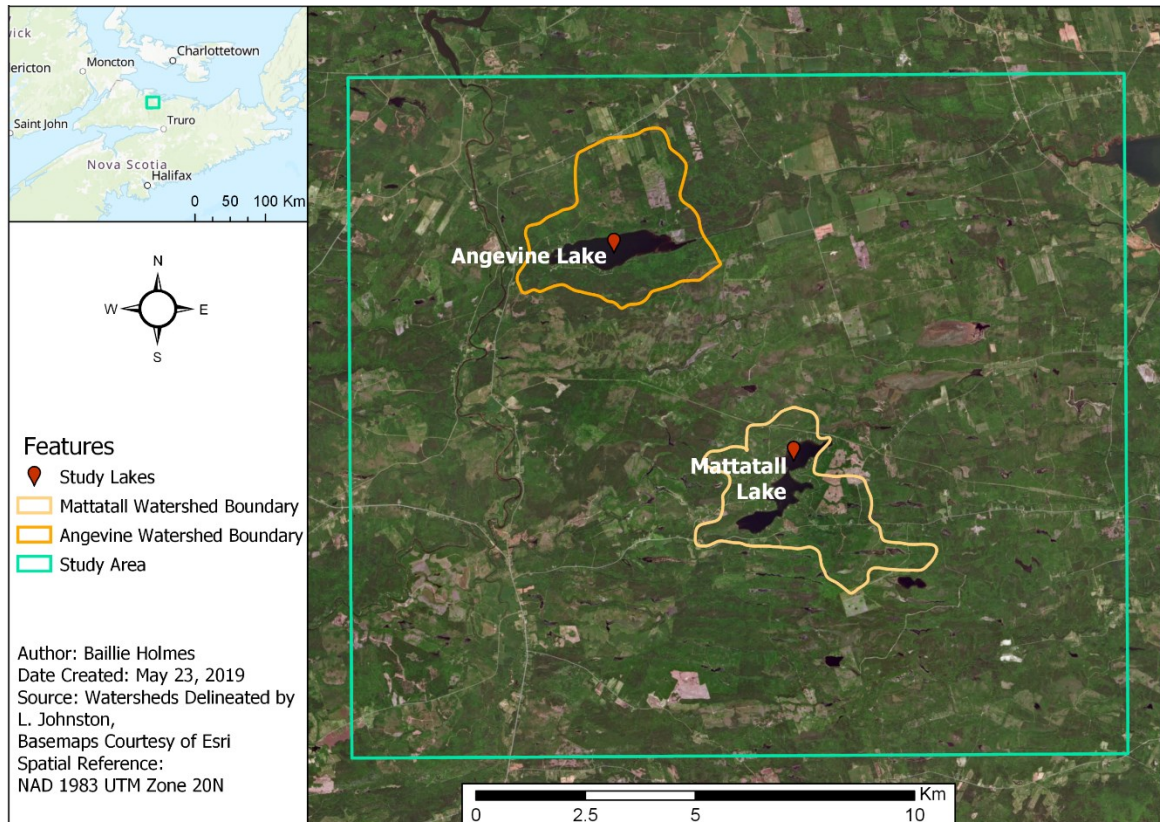
cyanobacteria can potentially produce anatoxin-a (Chernova et al., 2019) which is neurotoxic to humans, wild, and stock animals (Aráoz et al., 2010). Effects of toxicity from anatoxin-a can range from rashes and gastrointestinal upset, to tremors, respiratory paralysis and death depending on the dose/mode of exposure (Aráoz et al., 2010). Cyanobacterial HABs are therefore concerning from a public health and safety perspective in both recreational and drinking water lakes. Concern for what mechanisms led to the proliferation of *D. planctonicum* in Mattatall Lake, and whether it could be a continued issue, prompted this study.

Mattatall Lake (Figure 1.1) has a surface area of approximately 118.6 ha, with an 892 ha catchment (excluding the lake). It has a unique morphometry comprising three basins in series with constricted flow between them (Figure 1.1). The shoreline of Mattatall Lake is developed around the entirety of the lake with a mix of seasonal and permanent residential properties. Other land uses throughout the watershed have included forest harvesting and some agricultural activity.

The morphometry of Mattatall Lake was identified as a potentially pertinent factor in the formation of the HABs because two of the HABs originated from the southern most basin (CWRS, 2017). Therefore, a reference lake with similar water quality and watershed characteristics was selected to understand how a more typical single-basin lake has responded to similar regional/catchment development stressors. Angevine Lake was selected for this purpose. It is located 6.7 km from Mattatall Lake; has similar catchment characteristics in terms of forest cover, geology, and soil; has been affected by similar land alterations and regional stressors; and preliminary water sampling of the lakes indicated similar water chemistry (CWRS, 2017).

Angevine Lake (Figure 1.1) has a surface area of 151 ha, with a 997 ha catchment (excluding the lake). The shoreline of Angevine Lake is partially developed with seasonal and permanent residential properties. 270 ha of land to the south of the lake is a designated nature reserve, and includes 1200 m of protected shoreline (Nova Scotia Environment, 2017). Other land uses in the watershed have included agricultural activities and forest harvesting.





**Figure 1.1: Map of the study area including Mattatall and Angevine Lakes and their respective watershed boundaries.**

### 1.3 Thesis Objectives

Mattatall Lake has not had an observed HAB since the onset of this study in 2018. Prior to the HAB events, Mattatall Lake would have been regarded as possessing low risk of eutrophication given that this area is not heavily developed by urban or agricultural land uses. The challenge of studying such a lake is that there is not an obvious change in the watershed or known direct input that appears to have spurred the HAB events, and there is no water quality data available both before and during the events. This contrasts with many HAB studies where the lakes are eutrophied and reliably bloom every year. Mattatall Lake offers the unique opportunity to study how long term, cumulative effects can influence deviations in productivity in a lake system. A multifaceted approach to studying the environmental changes at Mattatall Lake is required to parse what factors might have contributed to the HAB events. Considering these important attributes of this study, the following research question was posed:

**Can factors contributing to HABs in Mattatall Lake be identified using an integration of environmental change study techniques?**

Based on this research question, we established the following research objectives:

Objective 1: Compare the contemporary water quality and the history/extent of landscape disturbance of Mattatall and Angevine Lakes and their respective watersheds.

Objective 2: Explore the role of climate in regulating lake characteristics from a regional perspective.

Objective 3: Elucidate which factors could have led to the HABs in Mattatall Lake using a weight of evidence approach.

Objective 4: Utilize paleoenvironmental data in combination with water quality monitoring, modelling and reference site comparison and assess the efficacy of using these tools together.

## Chapter 2 Literature Review

### 2.1 Lake Characterization

Lakes are described and distinguished by standard characterization systems. This allows lakes to be described by their general physical, chemical and biological qualities.

Characterization is typically the first step in a lake study program because these characteristics are quick to determine, establish the expected biological and physical processes within the lake and enable comparison to other lakes. Two fundamental characteristics of a lake are the trophic state and mixing regime which are described in detail in the following section.

#### 2.1.1 Trophic State

Trophic status is a classification system based on nutrient concentrations and the biological productivity the lake is capable of sustaining (Dodds et al., 1998). The three basic trophic states that a lake could be categorized as are oligotrophic, mesotrophic and eutrophic. Oligotrophic lakes are low in nutrients, algal biomass and are generally clear watered with deep photic zones (Dodds et al., 1998). There are oligotrophic lakes that have low water clarity due to high total organic carbon (TOC) and humic acids which decrease water pH; such lakes have been referred to as dystrophic (Kerekes et al., 1989; Williamson et al., 1999). Eutrophic lakes exhibit high nutrient concentrations, support high algal biomass, low oxygen (hypoxia), and basic pH conditions (Dodds et al., 1998). Eutrophic lakes can develop HABs of noxious cyanobacteria which can lead to further lake water quality degradation. Mesotrophic lakes are an intermediate between the oligotrophic and eutrophic conditions. In the absence of human development and activity, lakes will naturally exist anywhere on the oligotrophic to eutrophic spectrum. Some lakes are inherently fertile due to naturally occurring high nutrient availability; this is often related to the type and weathering of bedrock and soils of the watershed. For instance, lakes in the undeveloped interior of British Columbia that have catchments underlain by P-rich deposits of Eocene volcanic rock have been recorded as having soluble reactive phosphorus (SRP) concentrations exceeding 250 µg/L and yearly algal blooms (Murphy et al., 1983).

Nutrient availability is the limiting factor for lake productivity and is therefore an important part of the trophic state definition. Key nutrients for primary producers are phosphorus (P) and nitrogen (N). Inorganic carbon in the form of bicarbonate can also be limiting, but is generally provided in sufficient quantities in lake systems through geogenic weathering and

diffusion of atmospheric carbon dioxide (Freedman, 2010). Production in any given lake can be limited by either or both P and N (Bunting et al., 2007; Schindler, 1977). Several studies have demonstrated that P limits productivity in most freshwater systems rather than N (Freedman, 2010; Levine & Schindler, 2011; Schindler, 1978; Schindler, 1990). This is related to P not having a significant atmospheric transport component, and therefore must be supplied from the watershed. In contrast N can diffuse from the atmosphere and even be fixed by some primary producers, namely cyanobacteria (Kelly et al., 2021). Consequently, controlling P influx into lake systems is often the focus of lake resource management.

In addition to nutrient concentrations, chlorophyll-a (chl-a) and Secchi depth (SD) are used to define trophic status. Chlorophyll-a is a pigment found in oxygenic photosynthetic organisms, and concentrations of this pigment have been found to reliably characterize algal biomass in lake pelagic zones (Lyche-Solheim et al., 2013). In order to interpret chl-a concentrations effectively, a high spatial and temporal sampling frequency is required to account for phytoplankton community variation through space and time. Secchi depth measures the depth at which a black and white disk disappears/reappears in the water column. This measurement is subjective and operator dependent but has been demonstrated to correlate with water clarity and trophic state in clear water lakes (Brezonik et al., 2019). Given the simplicity and efficacy of SD measurement, it is used ubiquitously in lake studies.

The Organization for Economic Co-operation and Development (OECD) conducted a large-scale study quantifying the relationships between chl-a, total P (TP), total N (TN), and SD in lakes of varying trophic state. A Canadian supplementary report by Janus and Vollenweider (1981) compared the OECD study to a suite of Canadian lakes. They found that the relationship between chl-a and TP were similar, and thus trophic state threshold limits based on TP concentrations were developed (Janus & Vollenwelder, 1981). These trigger ranges were adopted by the Canadian Council of Ministers of the Environment (CCME) and are used across Canada (CCME, 2004). Trophic state threshold limits are summarized in Table 2.1.

**Table 2.1: Summary of trophic state threshold limits. TP limits are from CCME (2004). Chlorophyll-a and Secchi depth limits are from Vollenweider and Kerekes (1982).**

Trophic status	TP ( $\mu\text{g/L}$ )	Chlorophyll-a ( $\mu\text{g/L}$ )		Secchi depth (m)	
		Mean	Max.	Mean	Max.
<b>Ultra-oligotrophic</b>	< 4	< 1.0	< 2.5	$\geq 12$	$\geq 6$
<b>Oligotrophic</b>	4 – 10	< 2.5	< 8	$\geq 6$	$\geq 3$
<b>Mesotrophic</b>	10 – 20	2.5 – 8.0	8 – 25	6 – 3	3 – 1.5
<b>Meso-eutrophic</b>	20 – 35	--	--	--	--
<b>Eutrophic</b>	30 – 100	8 – 25	25 – 75	3 – 1.5	1.5 – 0.7
<b>Hypereutrophic</b>	> 100	> 25	> 75	$\leq 1.5$	$\leq 0.7$

### 2.1.2 Thermal Mixing Regime

Thermal mixing regime refers to the pattern of lake temperature change within the water column throughout the year. Lakes in temperate regions (i.e. Nova Scotia) of sufficient depth are typically dimictic meaning that they “mix” twice a year following periods of stratification (Lennox et al., 2010). Stratification occurs in the summer months when air temperatures are high, resulting in the warming of the first several meters of the lake surface, this layer is known as the epilimnion (Freedman, 2010). Cooler, denser water sits below the epilimnion at the bottom of the lake in a layer known as the hypolimnion. The higher density of the hypolimnetic waters prevents mixing with above layers (Freedman, 2010). The epilimnion and hypolimnion are separated by a steep temperature and density gradient, this zone of rapid change is known as the metalimnion or thermocline. Oxygen and dissolved matter can diffuse across the metalimnion, but this process is slow (Freedman, 2010). Erstwhile organic material within the lake sediment or sinking from above water layers is decomposed, a process that depletes dissolved oxygen (DO) (Nürnberg, 1994). This can lead to hypoxic or anoxic conditions in the lake hypolimnion during stratification.

In the fall as the epilimnion cools with air temperatures, stratification is diminished and winds and/or storm events mix the hypolimnetic waters with overlying layers. Dimictic lakes will inversely stratify again in the winter months when ice covered, where the water column will cool upward toward the frozen ice surface. Dimictic lakes will mix again in the spring when the

lake ice thaws, thus completing the cycle (Freedman, 2010). Monomictic lake stratify/mix once a year, while polymictic lakes are typically shallow and do not stratify (Freedman, 2010).

## **2.2 Climate Change and Lakes**

Lakes are uniquely sensitive to changes in climate and landscape due to their fast turnover rates on an organismal to ecosystem scale (Adrian et al., 2009). As such, lakes have provided some of the earliest indications of the effect of current anthropogenic climate change through their integration, either directly or indirectly, of the influence of climate on the catchment (Adrian et al., 2009). Physical, chemical and biological limnological responses to climate change in temperate dimictic lakes will be discussed in the following section.

### *2.2.1 Physical Impacts*

The Intergovernmental Panel on Climate Change (IPCC) estimates that eastern North America has already experienced a 0.75-1.5 °C increase in average air temperature (Allen et al., 2018). Lake water temperatures are intrinsically related to local air temperatures and have been demonstrated to closely follow climate seasonality (Filazzola et al., 2020). Stratification and spring turn over timing can also be impacted by shifting the timing of ice-off to earlier in the spring (Šporka et al., 2006). Earlier spring turn over and lake warming leads to an earlier onset of summer stratification, increasing the duration of this event. Epilimnetic water temperatures in lakes have effectively tracked with warming trends in North America, especially in the summer months (Arhonditsis et al., 2004; Butcher et al., 2015). Hypolimnetic waters do not respond as predictably, with temperature trends showing little change on average (Pilla et al., 2020). Increased warming epilimnetic water influences the density gradient of the water column, creating a greater density difference between top and bottom water layers, and thereby enhancing stratification stability (Paerl & Huisman, 2008). This can induce long-term shifts in the time-period of stratification, thermocline depth, and turnover timing. These physical changes can impact nutrient cycling within the lake, oxygen concentrations in the hypolimnion and the distribution/composition of the biological community.

### *2.2.2 Chemical Impacts*

Lake water chemistry is partly determined by the terrestrial landscape surrounding the lake. Climate change alters precipitation (in terms of volume and intensity), weathering rates of bedrock/soil, and runoff from the landscape, thus altering the export of chemical constituents

from the catchment (Trenberth, 2011). Nutrient concentrations (N and P) could be altered as a result of these processes (Paerl & Huisman, 2009; Rogora et al., 2003). Attributing nutrient increases to increased weathering from climate warming has been demonstrated effectively in alpine lakes (Rogora et al., 2003). In a temperate setting like NS, disentangling climate driven nutrient influx from human and internal nutrient cycling mechanisms has not been explored.

Climate change has been found to have an evidential impact on dissolved organic carbon (DOC) concentrations in NS lakes (Zhang et al., 2010). A 2010 study utilized data from 55 lakes across 21 years and included 38 lakes in southern NS. Zhang et al. found that annual mean total solar radiation and monthly total precipitation explained 84 % of the variation in DOC across the study period. This indicates that DOC is responsive to climate forcing as it impacts the terrestrial environment, particularly in catchments where the DOC is supplied from allochthonous sources (Adrian et al., 2009; Zhang et al., 2010). Dissolved organic carbon concentrations have a major impact on the absorption of solar radiation within a lake, which has cascading effects on primary productivity (e.g. reduces productivity with increasing DOC), alters the bioavailability of some elements (phosphorus, iron and carbon), and complicates drinking water purification (Williamson et al., 1999). How climate change will alter DOC in lakes is regionally constrained but results in NS indicated that increased solar radiation reduces DOC, while increased precipitation increases DOC (Zhang et al., 2010). Lake recovery from acidification also interacts with these relationships in NS which will likely confound the effects of climate change, particularly in the highly acid rain impacted southern region of the province (Anderson et al., 2017).

Dissolved oxygen is another important parameter in lakes that can be altered by climate change. Concentrations of DO in lakes are influenced by water temperature and thermal structure (Hanson et al., 2006). As these physical parameters shift in response to climate, DO will shift as a secondary response. In temperate dimictic lakes, response to a warming climate has led to an increase in the duration and stability of summer stratification. Under these conditions, oxygen depletion in the hypolimnion is driven by biological oxygen demand relating to bacterial respiration and decomposition of sediment organic matter (Smol, 2008). Increased primary productivity from eutrophication or climate drivers can compound this effect and speed the rate of oxygen depletion. Hypolimnetic hypoxia is an important lake management issue because it

has been attributed to an increase in internal P load and exacerbating or prolonging algal bloom issues despite external P load control (Nürnberg, 1995; Paterson et al., 2017a), which is discussed in greater detail in section 2.3.1 *Internal Phosphorus Loading*. Additionally, hypoxia prevents fish and other biota from inhabiting deep, cold waters of lakes where traditionally they might find refuge from high temperature surface waters (Smol, 2008). This could have important ramifications to inland fisheries in NS where cold water habitat maintenance is essential to the stability of economically valuable salmonid populations (Kurek et al., 2012).

### 2.2.3 *Biological Impacts*

It has been well established that climate change has widespread and complex impacts on terrestrial and aquatic ecosystems. This includes lacustrine ecosystems where physical and chemical changes driven by climate have cascading impacts on the biological community hosted by these systems. To decouple climate impacts on biota from other factors such as resource availability, predation, human harvesting/pollution, and natural temporal variability is difficult (Adrian et al., 2009). Biota have numerous, and often poorly understood, responses to a variety of stressors, and these vary by species, location and space/time context. Despite these complications, planktonic organisms have been demonstrated to rapidly respond to temperature and DO alterations, and therefore, shift in community assemblage as climate has changed (Adrian et al., 2009; Enache et al., 2011; Michelutti et al., 2003). A paleolimnological study covering several lakes in the vicinity of Halifax, NS found that algal assemblages in 19 pristine lakes were consistent with limnological changes linked with climate warming (Ginn et al., 2015). Studies on how climate change might drive HABs found that cyanobacteria have a competitive advantage when epilimnetic water reaches temperatures in excess of 25 °C (Jöhnk et al., 2008; Paerl & Huisman, 2008), making warming water more susceptible to HABs. Tracking climate impacts on larger long-lived species becomes more complicated as their life history and movement between systems introduce more variables to consider. However, predictive modelling estimates that freshwater fish stocks in eastern Canada could suffer from major disruptions and further population depletion should average air temperature increase by 4.5 °C (Minns & Moore, 1992).



## 2.3 Trophic State Deviation

Trophic states of lakes can be altered by a variety of factors. This section will review factors which may define the risk of trophic state change in dimictic lakes. Emphasis will be placed on factors which alter trophic state in the direction of eutrophication.

### 2.3.1 Risk Factors

Identifying and quantifying factors that put a lake at risk for eutrophication and HABs has been an important component in the management of lake resources. When a lake eutrophies, remedial steps to reverse the process are challenging to implement and not always successful (Steffen et al., 2014). Identifying at risk lakes is imperative to preventing eutrophication and prioritizing the deployment of resources to manage these systems (Bennion et al., 2005; Johnston et al., 2021). Risk assessment integrates the comprehensive knowledge base of eutrophication drivers and applies this knowledge to existing lake/watershed systems to identify where action might be required.

Where HABs are an expression of eutrophy, the factors that control algal growth must be taken into consideration when determining risk. The two most basic necessities for pelagic algal and bacterial growth are light availability and nutrient availability (Brylinsky, 2004). In stratified lakes, algae/cyanobacteria are mixed in the epilimnion. Therefore, if the thermocline depth is shallow and sufficient nutrients are available, algae/cyanobacteria will proliferate (Brylinsky, 2004). In contrast, if the lake is deep and unstratified and/or the water colour is > 40 total colour units (TCU), algal/cyanobacterial growth will be suppressed by limited light availability (Brylinsky, 2004; Jones et al., 1988). Given the importance of light and nutrients, eutrophication risk assessment in NS has been focused on the drivers that might alter these two key parameters.

The baseload of nutrient input into lakes is defined by inherent watershed characteristics such as the bedrock geology, soil and climate. NS has variable geology such that watersheds underlain by slow weathering granitic and metamorphic rock are generally low in nutrients and pH, while areas underlain by sedimentary rock lead to lakes with relatively higher nutrients and pH conditions (Johnston et al., 2021). Therefore, lakes underlain by sedimentary units may be at greater risk. Interfaced over these inherent watershed qualities is human activity. It has been widely established that anthropogenic alterations to watershed landscape and wastewater/septic/stormwater discharge are associated with increasing P influx into lakes

(Kleinman et al., 2011; Schindler, 1977; Steffen et al., 2014). This cultural eutrophication has been observed in NS in both rural (Campbell, 2021) and urban settings (Ginn et al., 2015).

The within lake processes that contribute to HAB vulnerability include light penetration, stratification, and flushing rate. These are controlled by such inherent characteristics as the water colour, lake depth, morphometry, and flowrate into and out of the lake. Light penetration is controlled mainly by coloured DOC, where increasing DOC decreases light availability for primary production. In NS, DOC in lakes is typically from allochthonous sources and proportional to the surface area of wetlands in the watershed (Kerekes et al., 1989). Forest removal and other soil mobilizing activities can increase the export of DOC into the lake, whereas acidification can decrease DOC (Williamson et al., 1999; Yan et al., 1996). Increasing DOC can suppress algal growth and even mediate impacts of anthropogenic stressors, while decreasing DOC can have the opposite effect (Williamson et al., 1999). Thus, clear water lakes, and lakes that have stressors contributing to decreased DOC are at greater risk of eutrophication.

Lake depth contributes to the ability of the lake to stratify. Johnston et al. (2021) conducted a study on eutrophication vulnerability assessment using 5 study lakes in northern NS and determined that in this climate, a depth greater than 7 m is sufficient for stable stratification. Lake depth is an inherent characteristic that might only be altered from drought conditions, or impoundment. In terms of flushing rate, lakes with swifter flushing rates are generally lower risk of eutrophication because the water is not retained with enough time for algal growth to occur (Jones & Elliott, 2007). Kerekes (1975) found that among a set of lakes in southern NS, lakes with flushing rates  $> 7$  /yr were less vulnerable to pollution. This threshold was used in eutrophication risk screening by Johnston et al. (2021) successfully. Human activity in watersheds, such as the increasing area of impermeable surfaces or forest removal can alter flushing rates (Scott et al., 2019). This can destabilize the flow rate of the lake, creating periods of fast flushing, and periods of stagnation, though these effects are very site specific. Generally, though, stagnation of flow and drought conditions increase the risk of eutrophication (Paerl & Huisman, 2009).

### 2.3.2 *Internal Phosphorus Loading*

Phosphorus is deposited in the lake sediment in organic and mineral forms; these are diagenetically transformed into P adsorbed onto iron (Fe)-oxyhydroxides and other minerals

(Nürnberg et al., 2018). Excess P can then be supplied to the pelagic zone autochthonously through seasonal releases of P from the lake sediment. This is another important source of P that can enhance eutrophication, shift water bodies from P to N limitation and hamper efforts to restore eutrophied lakes (Nürnberg, 1994; Tammeorg et al., 2016).

Phosphorus release from lake sediment is typically associated with anoxia (when DO is < 1.0 mg/L) at the sediment-water interface (James et al., 2015; Nürnberg, 1994). In temperate dimictic and monomictic lakes, DO depletion is greatest during stratification. This is when the oxygen demand from the degradation of organic matter and bacterial respiration at the lake sediment surface is greater than the rate at which oxygen is replaced via diffusion from overlying layers (Smol, 2008). This can happen both in summer and winter stratification events. In oxic conditions P is adsorbed to Fe-oxyhydroxides, as the redox potential at the sediment water interface shifts toward anoxia, the Fe-oxyhydroxides are reduced, leading to the desorption of P (Nürnberg et al., 2018). The P is then free to move into hypolimnion in the form of soluble reactive phosphorus (SRP). When the lake later mixes, this SRP can be distributed into the photic zone where it is available for uptake by photosynthetic biological agents (Nürnberg, 1994).

There are many factors which contribute to the actual P retention vs. release from lake sediment that extend beyond redox controls. The ratio of Fe:P in the water column has an important role in dictating whether SRP can become entrained in surface water for biological uptake (James et al., 2015). Gunnars et al. (2002) found that when the hypolimnetic dissolved Fe:P ratio was > 2:1 (on a molar basis) and the water was reoxygenated the following reactions occurred:  $\text{Fe}^{2+}$  was oxidized and hydrolyzed to Fe-oxyhydroxide, SRP was swiftly scavenged by Fe-oxyhydroxides and these molecules eventually settled to the sediment. This cycle has been referred to as the ‘ferrous wheel’, and can be a principal control on whether hypolimnetic SRP will actually become available when resuspended (James et al., 2015). Notably, colloids of Fe-oxyhydroxides with adsorbed P can be detected as SRP when measured using the Murphy and Riley (1962) ascorbic acid colorimetric method (James et al., 2015). This can lead to misinterpretation of available SRP, especially if samples are taken soon after lake turn-over and Fe:P ratios are unknown. In contrast, when Fe:P ratio is low (< 2:1 molar), SRP will not

completely bind to Fe-oxyhydroxides and will be available for biological uptake (Gunnars et al., 2002; James et al., 2015).

Additionally, aluminium (Al) hydroxides can nearly permanently bind P in both watershed soils and in the lake sediment (Nürnberg et al., 2018). The presence of Al can therefore enhance P retention in lake sediment (Norton et al., 2006). Aluminium is especially effective at retaining P in nutrient-poor, low calcium (Ca) oligotrophic lakes (Norton et al., 2006). Additionally, Al can be leached into lacustrine systems when lakes and watersheds are acidified from acid rain (Nürnberg et al., 2018). Acid deposition in NS has been successfully reduced by air pollution reduction legislation in North America (Sterling et al., 2020). However, studies have indicated that freshwater system recovery has been lagging, especially with respect to Al concentrations which have continued to increase (Sterling et al., 2020). Implications of how this might influence P retention in soils and lakes in the future is unknown.

Lake sediment composition can also control P retention regardless of the redox conditions in the overlying water. This has been observed in a number of lakes where oxidation of hypolimnetic water did not effect internal P cycling (Gächter & Wehrli, 1998; Hupfer & Lewandowski, 2008; Levine et al., 1986). Sediment control relates to each lakes unique sedimentation of organic matter, P, Al, Fe and the sulfide production by diagenic processes (Gächter & Müller, 2003; Hupfer & Lewandowski, 2008). Generally, lakes with high Fe and low sulfate concentration are less likely to release P from the lake sediment, even under anoxic conditions (Gächter & Müller, 2003).

Internal P loading processes have been related to larger and more sustained cyanobacterial HABs (O'Neil et al., 2012; Paerl & Huisman, 2009). This is because internal P loading can initiate a positive ecosystem feedback loop. An increase in productivity (whether through increased internal loading or external loading of P) leads to increasing sedimentation of organic matter, this can increase the extent of hypoxia in the profundal zone, and subsequently, increase internal P loading (Vahtera et al., 2007). The P released via internal P loading is readily available for biological uptake and therefore provides ready fuel for another HAB cycle (O'Neil et al., 2012; Vahtera et al., 2007).

## 2.4 Applied Paleolimnological Assessment

For this thesis, sediment cores will be dated, and analysis will focus on proxies that will inform on productivity and geochemistry. The theory behind how these proxies are accumulated in the lake sediment, analyzed and interpreted will be discussed in the following section. A review of how sediment core data can be related to historical climate records is also discussed.

### 2.4.1 Radiometric Dating

Having an accurate chronology of when sediment was deposited is critical to the interpretation of sediment archives. Recently deposited sediments in lakes (0 – 150 years old) are typically dated using  $^{210}\text{Pb}$ , a natural radioactive isotope of lead (Pb) with a half-life of 22.3 years (Appleby, 2001).  $^{210}\text{Pb}$  is produced in the atmosphere as part of the  $^{238}\text{U}$  decay series (Appleby, 2001).  $^{210}\text{Pb}$  is deposited in lakes through precipitation and dry deposition. Once in the lake it is scavenged from the water column and deposited into the lake sediment (Appleby, 2001). It is assumed that this flux of  $^{210}\text{Pb}$  is constant and has been related to rainfall and geographical location.

### 2.4.2 Productivity

Productivity has been recorded and reliably tracked in lake sediments with the use of chl-a (Michelutti & Smol, 2016). Chl-a is a photosynthetic pigment that is used for oxygenic photosynthesis (Papageorgiou, 2007). It is essential for photosynthesis in some phytoplankton, cyanobacteria and macrophyte vegetation. This pigment reflects blue-green light and is therefore the source of green colour observed in plants, algae and bacteria (Papageorgiou, 2007).

In lakes, most primary producers, including those that contribute to HABs, use oxygenic photosynthesis and therefore contain chl-a. When these biota die, they will eventually fall into the lake sediment where they undergo degradation and incorporation into the lake sediment record (Carpenter et al., 1986; Leavitt & Hodgson, 2001). Although most of the algal/bacterial bodies will have disintegrated, the pigments (chl-a, derivatives and degradation products) will remain in the lake sediment (Leavitt & Hodgson, 2001). This residual chl-a may be considered a biochemical fossil that can trace the abundance of past primary productivity (Leavitt & Hodgson, 2001).

There are some processes within the lake water column that can disrupt detrital chl-a in the epilimnion from descending to be stored in lake sediment. Photodegradation is regarded as

having the greatest impact on chl-a survival because it can occur rapidly. Carpenter et al. (1986) found that detrital chl-a' (a derivative of chl-a) had a half life of  $0.52 \pm 0.05$  days in the photic zone. The implication is that pigments that remain suspended in the euphotic zone of the lake for more than a few days are mostly destroyed (Carpenter et al., 1986). Secondly, grazing biota in the water column (i.e. zooplankton) can also be responsible for pigment removal, though this can be highly variable by lake (Carpenter et al., 1986).

Multiple studies have demonstrated that reflectance spectroscopy is an effective method of obtaining concentrations of chl-a and its derivatives as apposed to high-performance liquid chromatography (Das et al., 2005; Michelutti et al., 2005; Michelutti & Smol, 2016). It is rapid, and non-destructive which is well suited to multi-proxy paleolimnological studies. Michelutti et al. (2010) demonstrated that visible ray spectroscopy (VRS) inferred chl-a effectively tracks trends in lake primary productivity and is not obscured by diagenic trends. They demonstrated this through sampling several lakes throughout North America (Ontario to Baffin Island) with well documented trophic histories and confirming that VRS chl-a followed these trends (Michelutti et al., 2010).

### 2.4.3 *Geochemistry*

Major elements that lake sediments are comprised of are equivalent to those most abundant in Earth's lithosphere, these include Al, silicon (Si), Fe, manganese (Mn), sodium (Na), potassium (K), titanium (Ti), Ca, magnesium (Mg), strontium (Sr), P and sulfur (S) (Cohen, 2003). Trace elements occur in low concentrations in lake sediment, and are more commonly used as indicators of anthropogenic pollution, these include: lithium (Li), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), cobalt (Co), vanadium (V), arsenic (As), molybdenum (Mo), Pb, mercury (Hg) and selenium (Se) (Cohen, 2003). Concentrations of both major and trace elements can vary naturally through the sediment archive. Accumulation of these elements can be altered, though, when processes that deposit them are interceded by anthropogenic activity or long-term geogenic/biogenic change.

Landscape change within a lakes watershed, whether by forest removal, shoreline development, road and infrastructure development, or even land cover changes can be tracked using elements commonly found in clay minerals (Boyle, 2001; Mackereth & Cooper, 1966). These elements include Na, K, Al, Ti and Si (Mackereth & Cooper, 1966; Nesse, 2012).

Generally, landscape alterations of the watershed increase erosion and export of clastic material (Cohen, 2003). This is recorded in the sediment sequence as relative increasing concentration of the aforementioned elements. Titanium has been identified as the best representation of landscape change because it is a conserved element (Cohen, 2003; McHenry, 2009). Titanium does not often participate in chemical weathering reactions, does not have a major atmospheric transport mechanism, and is insoluble in most conditions (i.e. acidic to circum-neutral freshwater; McHenry, 2009). Titanium has been used in many paleolimnology studies in NS to track landscape change, and results have been strongly related to known disturbance mechanisms in each lake's respective watershed (Davidson et al., 2021; Dunnington et al., 2018; Tymstra et al., 2013). Therefore, the main source of Ti to lake sediments is from direct transport and deposition of clastic material.

Elements can also be deposited into the lake, and subsequently the lake sediment, via atmospheric deposition. Stable Pb, Hg and V are examples of elements where accumulation in lake sediment has been closely related to atmospheric deposition mechanisms (Charles et al., 1990; Cohen, 2003; Dunnington et al., 2018). Stable Pb is of particular interest because most lakes proximal to human habitation share a characteristic Pb curve associated with the combustion of leaded gasoline and augmented by longer range transport of industrial pollution (Gallagher et al., 2004). Leaded gasoline was discovered in 1921 (though the actual onset of public usage varies across North America), and the product was subsequently phased out in the 1980s (Nriagu, 1990). Therefore, lake sediment cores typically have a peak concentration of Pb associated with the local peak usage of leaded gasoline, followed by a decline toward more modern sediments (Boyle, 2001; Dunnington et al., 2018; Gallagher et al., 2004). Dunnington et al. (2018) evaluated anthropogenic Pb atmospheric deposition in lakes across eastern North America (from Adirondack Mountains in New York, USA to NS, Canada). It was found that the Pb from gasoline may be the most important source in NS, rather than other industrial sources/long-range transport (Dunnington et al., 2018). Other work from these authors has indicated that the timing of peak leaded gasoline usage in NS is 1970-1990 (Dunnington, 2017).

Redox conditions at the bottom of the lake water column can affect the sequestration of certain elements. Redox state changes can either liberate or increase sequestration of some metals and nutrients (Cohen, 2003). Iron and Mn are particularly redox sensitive, both elements

are chemically similar (appearing side-by-side on the periodic table), but Mn dissolves more readily under reducing conditions, therefore the ratio of Mn:Fe can be useful in determining past redox conditions (Davison, 1993; Engstrom & Wright, 1984; Naeher et al., 2013). However, the cycling of these elements is complex and related to many factors that can often be site-specific like microbial activity, sediment composition and photo-chemical reactions (Davison, 1993). Iron and Mn redox driven sequestration can also be obscured by clastic deposition if these elements are present in the parent bedrock and soils of the watershed (Makri et al., 2021). Studies focussing on Mn sequestration have found that there are other processes this element can be indicative of. Schaller et al. (1997) found that Mn concentration peaks can record rapid oxidation events. Sudden artificial oxidation of a sediment surface led to a particulate Mn flux coming out of solution and being partially preserved in the lake sediment (Schaller et al., 1997). Koinig et al. (2003) were able to correlate Mn with organic matter accumulation. It was hypothesized that Mn concentrations could be controlled by reducing conditions caused by an increase in organic matter supply and subsequent oxygen depletion from organic matter degradation (Koinig et al., 2003). In summary, when using Fe and Mn as redox indicators it is important to consider the unique context of the lake being studied given the complexity of how these elements are deposited.

#### *2.4.4 Linkage with Climate Records*

The use of historical instrumental climate records alongside paleolimnological datasets is useful in determining correlations among climate variables and shifting abundances of certain paleolimnological indicators. Climate datasets differ inherently from paleolimnological datasets, making comparison challenging. While climate data has clearly resolved time intervals (ex. air temperature recorded as daily, monthly or annual averages), the time interval represented by lake sediment sections can vary depending on compression and changing sedimentation rates (Paterson et al., 2017a). This means that any given sediment interval may represent one or several years of accumulation and dating of the sediments is not as accurate as climate records. Climate data therefore requires careful summarization in order to achieve optimal comparability with sediment core data.

Indirect comparison is a simplistic and qualitative approach that may be applied if statistical analysis is not a priority. This method was demonstrated by Michelutti et al. (2003)



when studying diatom responses to recent climatic changes in a lake in Nunavut, Canada. The authors assembled a long-term climate record and examined temperature and precipitation averages on a seasonal basis. They had found that diatom community assemblages had shifted consistently along with general climate changes from 1988 to 1997 (Michelutti et al., 2003). Favot et al. (2019) had a similar approach when studying productivity changes in a remote oligotrophic lake in northern Ontario. They used linear regression to summarize the rate of change in climate records across the whole time series (Favot et al., 2019). The climate analysis was interpreted alongside various biological indicators with the assumption that the lake hasn't been significantly impacted by anthropogenic activity (Favot et al., 2019). Enache et al. (2011) core sampled several lakes in the remote and undisturbed Experimental Lakes Area of northern Ontario and analyzed for a range of biological proxies. These proxies were interpreted alongside water quality data and climate data. Statistical methods were used to understand water quality and biological indicator relationships, but assuming significant anthropogenic impacts had not occurred, authors qualitatively compared their findings to the climate records (Enache et al., 2011). It was found that biological responses to climate warming varied among the lakes depending on morphometry and water quality (Enache et al., 2011).

## Chapter 3 Methodology

### 3.1 Climate Data Retrieval and Analysis

Climate data was gathered from Environment and Climate Change Canada (ECCC) weather station historical records. A record > 100 years was needed, so weather stations were selected based on proximity to the study area and duration of time the record covered. Stations that consistently recorded longer timespans of weather data (multiple decades) were favoured over ephemeral stations that only recorded a few years. The selected stations based on these criteria are described in Table 3.1. Three stations have existed in Truro NS since 1872 in close proximity to each other and less than 50 km away from the study area. The Truro NS records ended in 2002, and therefore were supplemented by Debert NS station records which began recording in 2003 at a closer proximity to the study area. In total, these stations provided a 148-year record of daily temperature, precipitation, and maximum wind gusts (Table 3.1). The Truro NS stations 6490 and 6491 were located in the same place, therefore these stations were favoured in the years that overlapped with Truro NSAC NS 6492.

**Table 3.1: Selected ECCC weather stations, their relative distances from Wentworth, NS, and duration of record.**

Station Name	Station ID	Distance (km)	Duration of Record	Total Years Available
Truro NS	6490	35.6	1872 – 1915	43
Truro NSAC NS	6492	33.8	1910 – 1966	56
Truro NS	6491	35.6	1960 – 2002	42
Debert NS	42243	22.7	2003 – 2020	17

Mean daily minimum air temperatures were calculated for annual (12-month average), summer (June, July, August), fall (September, October, November) and winter (December, January, February) intervals for every year in the 148-year record. Daily minimum air temperatures were selected for analysis because they demonstrate the most pronounced increases over time across Canadian weather stations (Vincent et al., 2012) and, on an annual basis, have a profound impact on lake ice coverage (Filazzola et al., 2020). Linear regression was applied to the annual, summer, fall and winter mean daily minimum air temperatures to determine whether daily minimum air temperatures have increased across the record. Slopes were checked for

significance (where  $p < 0.05$  was considered significant) prior to calculation of the net change in temperature.

Total daily precipitation was summed for every year in the 148-year record. Linear regression was applied to the yearly total precipitation to determine whether precipitation has changed across the 148-year record. The slope was checked for significance (where  $p < 0.05$  was considered significant) prior to calculation of the net change in precipitation.

Daily maximum wind gust was the only windspeed parameter available across the Truro and Debert datasets. This parameter was not consistently reported, having one cluster of records from 1970 – 1990 from the Truro NS 6491 station and a second cluster from 2000 – 2020 from the Debert NS 42243 station. The available records were averaged for each year, and visual inspection indicated that the wind gust records were highly influenced by station location (Appendix A). Therefore, it was concluded that the windspeed records do not reliably predict changes in windspeed on a climactic scale given the limited data available; therefore these data were forsaken from further analysis/consideration.

## **3.2 Lake Water Sampling**

### *3.2.1 Lake Morphometry*

The bathymetry of Mattatall and Angevine Lakes was surveyed using point-by-point depth sounding devices. Mattatall Lake's bathymetry was mapped by Dunnington and Redden in 2018 using a Humminbird Helix 9 sounder with 83/200 Hz dual beam transducer (Johnson Outdoors, Inc., Racine, Wisconsin, USA).

Angevine Lake bathymetry was determined using a Garmin echoMAP 50 dv combination fish finder/chart plotter (Garmin International, Inc., Olathe, Kansas, USA). The coordinates and associated depth measurements were imported as point features into ArcGIS Pro 2.3.0 (ESRI Inc., 2018). The waterbody boundary for Angevine Lake was obtained from the NS Topographic DataBase (1:10 000 scale; Government of Nova Scotia, 2021), and imported as a polyline feature into ArcGIS and assigned a reference depth of 0 m. The spot depths and waterbody boundary were then used to construct a digital elevation model (DEM) using the Topo to Raster tool. The DEM was then used to create contour lines with the Contour tool, which connects cells of equal elevation with a line.

Lake volume was calculated using the Surface Volume tool in ESRI ArcMap 10.3.1. The volume was calculated between the DEM of the lake bathymetry and a reference surface of 0 m. Hypolimnetic water volume was calculated by creating a reference surface at the depth of the top of the hypolimnion for each lake in the summer sampling event. For the purpose of this study, the top of the hypolimnion was defined as the end of the thermocline, where the difference of temperature values between measurements was  $< 1$  °C. The volume was calculated between the DEM of the lake bathymetry beneath the top of hypolimnion reference surface.

Lake flushing rate was calculated using the following formulas:

$$\text{Flushing rate} = \frac{Q}{V}$$

$$Q = (A_{ws} * P_r * RC) + ((P_r - E) * A_l)$$

where Q is the predicted outflow ( $\text{m}^3/\text{yr}$ ), V is the volume of the lake ( $\text{m}^3$ ),  $A_{ws}$  is the area of the watershed ( $\text{m}^2$ ),  $P_r$  is the average annual precipitation ( $\text{m}/\text{yr}$ ), RC is the average runoff coefficient, E is the lake evaporation ( $\text{m}/\text{yr}$ ) and  $A_l$  is the area of the lake ( $\text{m}^2$ ). Values for average annual precipitation, evaporation and runoff coefficient were based on long-term (20-year) climate averages for the region and calculated by Johnston et al. (2021) for both Mattatall and Angevine Lakes. For both lakes, the  $P_r$  was 1.239  $\text{m}/\text{yr}$ , E was 0.5  $\text{m}/\text{yr}$  and RC was 0.7 (Johnston et al., 2021). The value of Q is assumed to include all surface water and groundwater inputs into the lake.

### 3.2.2 *Water Quality Monitoring*

Lake water quality at Mattatall and Angevine Lakes was established using parallel sampling and analysis techniques. Sampling events occurred on the same day for both lakes across the open water seasons in 2018 and 2019. Data was gathered from the water column at the deepest location in both lakes (Figure 3.1 and 3.2). Two additional locations were sampled at Mattatall Lake at the centre of the other two basins (Figure 3.1). Each sampling event took samples from the surface and bottom of the water column with several discrete samples in-between. The amount and depth of samples were decided based on the thermal stratification structure of the lake at the time of sampling.

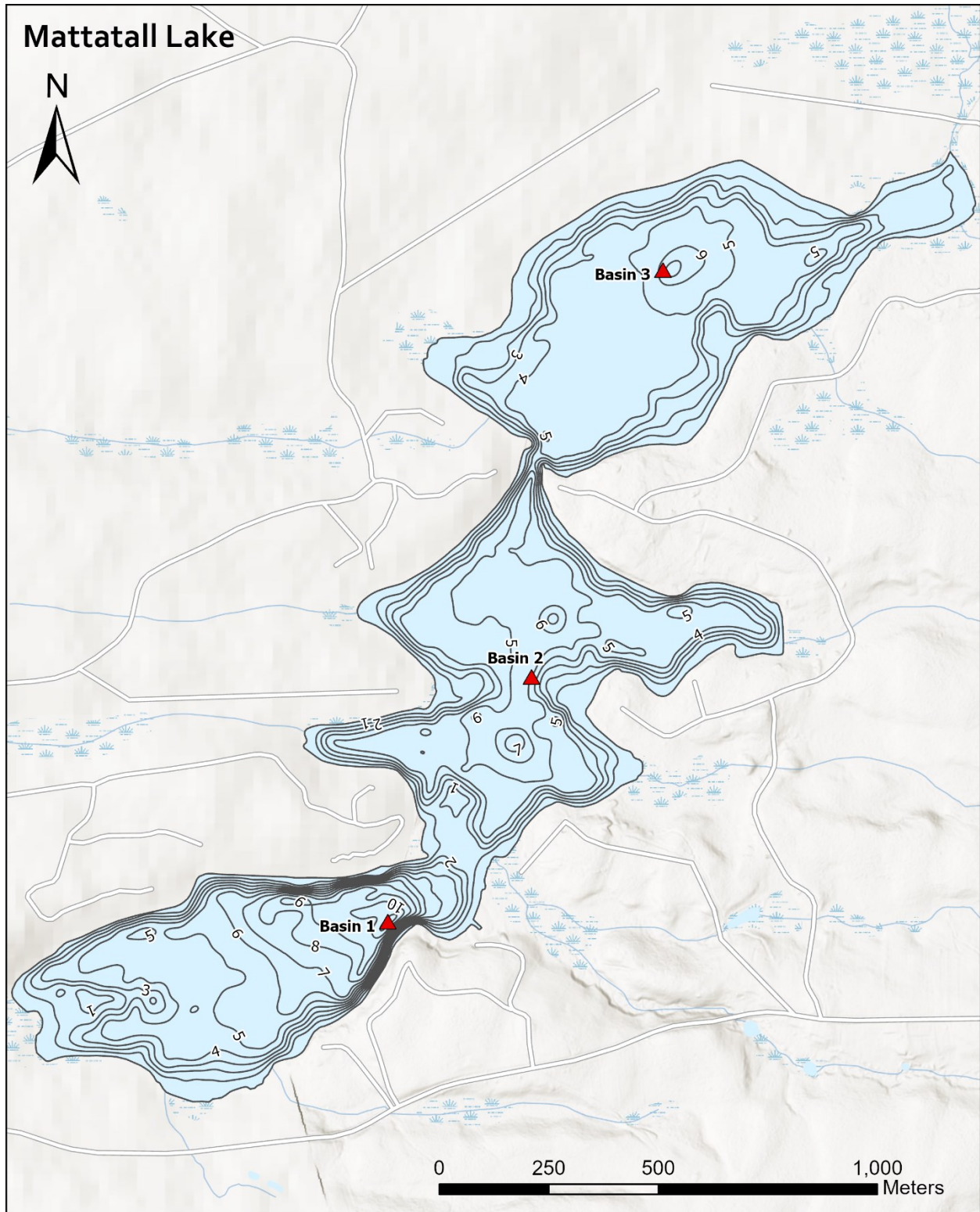
Clean polyethylene sample bottles were triple rinsed in lake water prior to sample collection. Surface samples were taken by submerging and filling the sample bottle 50 cm below water surface. Grab samples at lower depths in the water column were taken using a 2.2 L PVC Kemmerer sampler. A portion of the lake water samples were volume weighted immediately following lake sampling and submitted to Bureau Veritas Bedford Environmental Laboratory in laboratory provided sample containers. Volume weighted samples were analyzed for a suite of parameters in the Routine Comprehensive Package analysis which included the following parameters:

- pH
- Total Alkalinity (as CaCO<sub>3</sub>)
- Bicarb. Alkalinity (as CaCO<sub>3</sub>)
- Carb. Alkalinity (as CaCO<sub>3</sub>)
- Conductivity
- Turbidity
- Colour
- Calculated TDS
- Hardness (as CaCO<sub>3</sub>)
- Total Sodium
- Total Potassium
- Total Magnesium
- Total Calcium
- Dissolved Sulphate
- Dissolved Chloride
- Reactive Silica
- Nitrate-Nitrite (as N)
- Nitrogen (Ammonia)
- Orthophosphate (as P)
- Total Phosphorus
- Total Organic Carbon
- Langelier Index (@ 20C)
- Langelier Index (@ 4C)
- Saturation pH (@ 20C)
- Saturation pH (@ 4C)
- Anion Sum
- Cation Sum
- Ion Balance (% Difference)
- Total Aluminum (Al)
- Total Antimony (Sb)
- Total Arsenic (As)
- Total Barium (Ba)
- Total Beryllium (Be)
- Total Bismuth (Bi)
- Total Boron (B)
- Total Cadmium (Cd)
- Total Chromium (Cr)
- Total Cobalt (Co)
- Total Copper (Cu)
- Total Iron (Fe)
- Total Lead (Pb)
- Total Manganese (Mn)
- Total Molybdenum (Mo)
- Total Nickel (Ni)
- Total Phosphorus (P)
- Total Selenium (Se)
- Total Silver (Ag)
- Total Strontium (Sr)
- Total Thallium (Tl)
- Total Tin (Sn)
- Total Titanium (Ti)
- Total Uranium (U)
- Total Vanadium (V)
- Total Zinc (Zn)

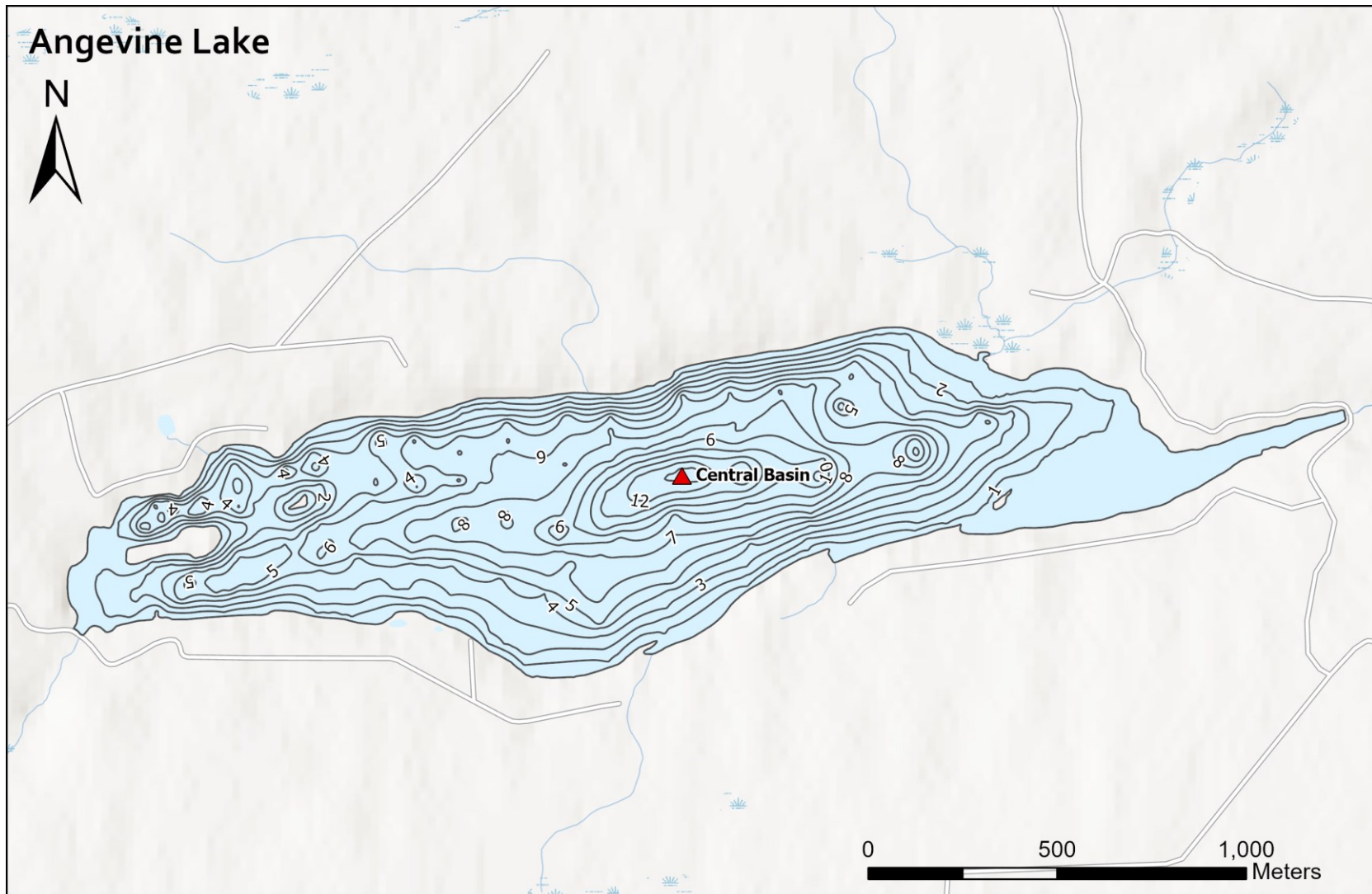
Chlorophyll-a, TP and SRP was analyzed at discrete depths. Chlorophyll-a samples were submitted to Dalhousie Oceanography Micro-Algal Production and Evaluation Laboratory and analyzed using the acidification (Lorenzen and Jeffrey, 1980) and Welschmeyer (Welschmeyer, 1994) methods within 24 hrs of collection. These methods were modified slightly for freshwater media by extracting pigment with a 3:2 mixture of 90 % acetone:dimethyl sulfoxide. This mixture is effective in extracting pigment from species with thicker cell walls that are more commonly found in freshwater systems (Shoaf & Lium, 1976). Total phosphorus and SRP samples were analyzed at Dalhousie Centre for Water Resources Studies (CWRS) within 24 hrs of collection using the ascorbic acid digestion method described by Murphy & Riley (1962) for a low concentration detection range of 0.001 – 0.350 mg/L.

### 3.2.3 *In-situ* Measurements

*In-situ* water column temperature (°C), DO (percent and mg/L), conductivity (µS/cm) and pH were measured during each water sampling event at the locations referred to in Figure 3.1 and 3.2. Measurements were taken using a YSI Model 600 sonde (YSI Inc., Yellow Springs, OH, USA) with 30 m cable at 1 m intervals of depth until 0.2 m above the bottom of the lake to avoid sediment disturbance. The YSI sonde pH and conductivity sensors were calibrated yearly, and the DO sensor was calibrated before each use. Secchi depths were taken using a 20 cm weighted Secchi disc to measure water transparency. The euphotic zone was calculated as 2.5 x SD (Green et al., 2015). Profiles taken at spring, summer and fall sampling events were selected for visualization in this thesis. The summer and fall sampling events selected were August 9, 2018 and October 17, 2018, respectively for both lakes. Spring sampling events took place on May 8, 2018 for Mattatall Lake and April 22, 2019 for Angevine Lake. Profiles for chl-a, TP and SRP from samples taken on the same days were also graphed in profile to observe changes in these parameters alongside the *in-situ* measurements.



**Figure 3.1: Sampling locations and bathymetry of Mattatall Lake. Water quality sampling and in-situ measurements were taken at Basin 1, 2 and 3. A gravity core was collected at Basin 1. Water depth contours are shown at 1 m intervals..**



**Figure 3.2: Sample location and bathymetry of Angevine Lake. Water quality sampling, in-situ measurements, and gravity core collection all occurred within the Central Basin. Water depth contours are shown at 1 m intervals.**



### 3.3 Landscape Change

#### 3.3.1 Landsat Imagery Collection

Imagery covering the study area (Figure 1.1) were collected from the U.S. Geological Survey (USGS) Earth Explorer website (USGS, n.d.). The datasets for Landsat 5, 7 and 8 were selected at Collection 1, Level 2 to obtain images that have had been atmospherically corrected. Summer imagery with less than 10 % cloud cover was selected at approximately 8-year intervals between 1985 and 2018. With an additional image from October 2016 because a major clear cut and algal bloom event in Mattatall Lake occurred in this year (Table 3.2).

**Table 3.2: Metadata of Landsat Images used.**

Date	ID	Landsat Satellite	Path	Row
1985/07/28	LT05_L1TP_008028_19850728_20170219_01_T1	4-5 TM	8	28
1993/08/19	LT05_L1TP_008028_19930819_20170117_01_T1	4-5 TM	8	28
2002/07/19	LE07_L1TP_008028_20020719_20170129_01_T1	7 ETM+	8	28
2009/08/15	LT05_L1TP_008028_20090815_20161022_01_T1	4-5 TM	8	28
2016/10/16	LC08_L1TP_008028_20161005_20170320_01_T1	8 OLI/TIRS	8	28
2018/07/07	LC08_L1TP_008028_20180707_20180717_01_T1	8 OLI/TRS	8	28

#### 3.3.2 Landcover Change Digitization

Land cover change in each image was manually digitized into polygons using an infrared visualization to increase the contrast between vegetation and deforested areas. A feature was added to the attribute table of the polygon denoting the year of the imagery it was sourced from.

#### 3.3.3 Application of Normalized Difference Vegetation Index

The Normalized Difference Vegetation Index (NDVI) was applied to each Landsat image using the Model Builder on ArcGIS Pro (Appendix A). The Visible Red (R) and Near Infrared (NIR) Bands from the Landsat files were input into the Raster Calculator. In the Raster Calculator the inputs were processed using the standard NDVI equation (Kriegler et al., 1969):

$$NDVI = \frac{NIR - R}{NIR + R}$$

The result of the calculation gives each cell a number between -1 and +1. Values near -1 indicate greater red reflection than NIR reflection, and thus, ground vegetation is unhealthy (ESRI Inc., n.d.). Values near +1 indicate greater NIR reflection than red reflection, indicating that vegetation is healthy (ESRI Inc., n.d.). To visually represent changes from one photo to the next through time, the NDVI raster from 2 subsequent satellite images were merged into a composite band layer.

A second approach was applied to better quantify forest cover variation. The model builder was used to again calculate the NDVI of two images. The two layers were then subtracted using the Raster Calculator. The resulting raster was then applied to the Greater Than Equal tool, which reclassified cells according to whether a logic statement is TRUE (1) or FALSE (0). The cells were reclassified according to whether they were greater than or equal to -0.1 or not. The value -0.1 was selected through a trial-and-error process of detecting significant forest removal that was apparent in the raw imagery and composite band layers. The model (Appendix A) was designed to output separate rasters for Mattatall Lake watershed and Angevine Lake watershed such that the deforestation areas could be contrasted. Following processing, cell counts were taken from the attribute tables of the rasters to calculate the total area of each class (deforested or vegetated).

#### *3.3.4 Uncertainty*

There is inherent uncertainty associated with using Landsat surface reflectance imagery, mainly relating to resolution. Firstly, with respect to spatial resolution, the reflectance rasters are limited by a 30 x 30 m cell size. At this spatial resolution, details such as the exact perimeter of deforestation can be obscured. This limitation was disregarded due to the watershed scale of this study, and, because exact measurements were less important than understanding relative deforestation in two watersheds.

Secondly, Landsat data was retrieved from three different satellites. This created uncertainty relating to variable radiometric resolutions when comparing images from Landsat 5 to Landsat 7 or 8. Due to the range of study years, obtaining images from only one satellite was not possible since Landsat 5 was discontinued in 2013 (USGS, n.d.). The images originating from Landsat 8 have a greater radiometric resolution and slightly different band widths with respect to the R and NIR bands used for this study as compared to Landsat 5 and 7. This may

have added a slight bias to resulting NDVI calculations and comparisons among different satellite imagery.

Thirdly, due to the nature of the images being dispersed and discrete captures in time, there is temporal resolution uncertainty. The evidence of deforestation in each image is closely related to how soon the activity took place before the image was captured. Some activity, especially at smaller scales, may not have been captured in this study.

### **3.4 Sediment Sampling**

Sediment cores were retrieved from Mattatall Lake on March 14, 2019 and from Angevine Lake on July 24, 2019 using a Glew gravity coring device (Glew, 1989). The cores were taken at the deepest point of each lake which was identified with bathymetric mapping (Figure 3.1 and 3.2). The cores were extruded directly following collection using a Glew portable extruding device (Glew, 1989) at 0.5 cm intervals. Sediment sections were then refrigerated at 4 °C until further processing.

### **3.5 Sediment Analysis**

Sediment sections from Mattatall and Angevine Lakes were analyzed in parallel. All analyses required dried sediment, so samples were dried for 48 hr at approximately 60 °C. Samples were weighed before and after drying to obtain water percentage and dry density of the sediment sections. The samples were then crushed and powdered with an impermeable clay mortar and pestle. Dried samples were placed in 60 mL plastic snap-cap vials and stored at room temperature until further analysis.

#### *3.5.1 <sup>210</sup>Pb Dating*

Dried sediment samples from Mattatall and Angevine Lake cores were sent to the Paleoecological Environmental Assessment and Research Laboratory (PEARL) at Queens University in Kingston, Ontario. Samples were selected spanning the length of both cores, 15 from Mattatall Lake and 13 from Angevine Lake. Samples were prepared using methods described by Schelske et al. (1994). A germanium crystal detector was used to measure the gamma activities of the radioisotopes <sup>210</sup>Pb and Cesium 137 (<sup>137</sup>Cs). The constant rate of supply (CRS) model was then applied to estimate ages of the sediment intervals (Appleby, 2001).

### 3.5.2 *Total Metals*

All dried sediment section samples from the Mattatall and Angevine Lake cores were analyzed for total metals using portable X-ray fluorescence (XRF) at Acadia University. The XRF device used was a Panalytical Epsilon 1 (Malvern Panalytical, Ltd., Malvern, United Kingdom) on the Lake Sediment Total program. The Lake Sediment Total program was developed using certified reference materials (CRMs) and internal standards that had been calibrated with inductively coupled plasma mass spectroscopy. Calibration of the Lake Sediment Total program followed methods established by Dunnington et al. (2019). Dried samples were kept in their 60 mL plastic vials, the cap was removed, and a plastic wrap film was secured to the top of the vial. The vial was then inverted over the x-ray window for approximately 3-4 minutes as analysis took place. Blanks and CRMs were used every session to ensure instrumental drift had not occurred. Every fifth sample was measured in triplicate to measure the precision of measurement for each element. The Lake Sediment Total program provided concentrations of 41 elements. Metals selected for this study included total P, Fe, Mn, Pb and Ti. Phosphorus was selected to indicate past nutrient concentrations in the lake; Fe and Mn were selected to indicate redox shifts through time; Pb was selected as an indicator of atmospheric Pb deposition from combustion (and therefore human settlement); and Ti was selected as an indicator of clastic sediment input from the watershed.

### 3.5.3 *Chlorophyll-a*

Dried sediment samples from the Mattatall and Angevine Lakes cores were prepared for VRS chl-a analysis by sieving the dried sediment through a 125  $\mu\text{m}$  filter. Sieving was necessary to remove large particles that could influence the spectral qualities of the sediment (Michelutti & Smol, 2016). Approximately half of the samples from each core were selected (every second sample down the length of each core). Approximately 1  $\text{cm}^3$  of sieved samples were then placed in 11.1 mL glass shell vials. Samples were sent to PEARL for analysis using a Model 6500 series Rapid Content Analyzer spectroradiometer, as described in Michelutti & Smol (2016). This method assumes that chl-a and its degraded products (chlorins) have similar spectral qualities, and therefore a bulk estimation of total chl-a can be inferred (Michelutti & Smol, 2016).

#### 3.5.4 *Statistical Methods*

All graphing and statistical analysis was completed using R (R Core Team, 2021). Principal components analysis (PCA) was applied to the sediment chl-a and geochemistry data to explore potential similarities and dissimilarities in the biogeochemistry of the Mattatall and Angevine Lake sediments across the entirety of both archives. Summarizing of the variables showed there were no zeros in the dataset. Each variable was then tested for normality using the Wilkes-Shapiro test (Peck, 2016), all were found to be not normal. Manganese was particularly skewed, so this variable was removed. The data was then centered and scaled to improve normality using the z-score method (Peck, 2016). Finally, PCA was applied to the data using the `princomp()` package and the default correlation matrix (R Core Team, 2021).

General linear models (GLM) were applied to determine whether certain variables, or combinations of variables, were statistically correlated with chl-a in both lakes. Chlorophyll-a was treated as the dependent variable, while Ti, Fe, P and Pb were treated as independent variables. Manganese was not included because those data were heavily skewed. Before a model was created, the data was checked for collinearity using pair plots and correlation coefficients. Following this check, only uncorrelated variables were used in the model. The resulting model was then checked for accuracy using the adjusted  $R^2$ . The model was then tested to ensure the assumptions of multivariate regression were satisfied. Assumptions and corresponding statistical tests were applied following the methods described by Field et al., (2012). The assumptions of multivariate regression and their corresponding tests are described below:

1. Existence – This is assumed to be true and was not tested.
2. Independence – That the predictor variables are independent of each other. This was tested using the Durbin-Watson test, where the null hypothesis is that variables do not autocorrelate.
3. Linearity – There is a linear relationship between the dependent and independent variables. This was tested using Ramsey's RESET test, where the null hypothesis is that there is linear relationship among the data.
4. Homoscedasticity – That all variables have similar variation across all observations. This was visualized using a residuals vs. fitted plot, and tested using the Breusch-Pagan test, where the null hypothesis is that variances are equal.

5. Normality – That all variables have a normal distribution. This tested using the Shapiro-Wilk's test where the null hypothesis is that the data are normal.
6. X is measured without error – This is assumed to be true and was not tested.

Following assumption tests, both a forward and backward stepwise regression (Field et al., 2012) was applied to obtain a more efficient model using a subset of the independent variables. The efficiency of the output models was assessed using Akeike information criterion (AIC; Field et al., 2012), and the accuracy of the models was assessed using the adjusted  $R^2$ .

## Chapter 4 Results and Discussion

### 4.1 Weather and Climate

Air temperature and precipitation data sourced from proximal ECCC weather stations in Truro and Debert, NS are summarized in the following sections. Windspeed data was insufficient for analysis, and was highly dependent on the weather station location rather than following regional patterns, as shown in Appendix A.

#### 4.1.1 Air Temperature

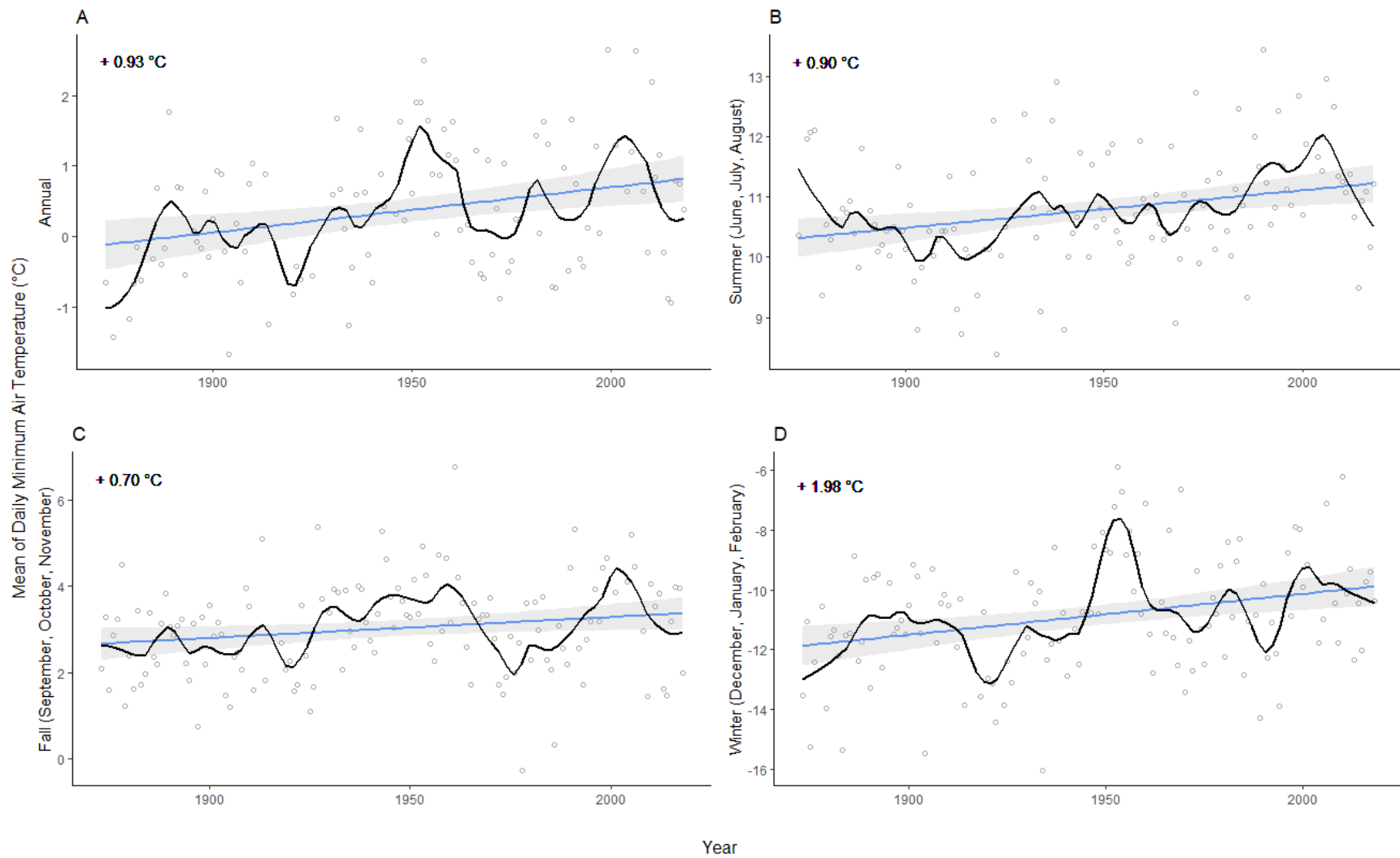
A 148-year record of daily minimum air temperatures are summarised in Figure 4.1. Linear regression analysis found that for the Annual, Summer, Fall and Winter means, the mean daily minimum air temperature has increased by 0.93, 0.90, 0.70 and 1.98 °C, respectively (Figure 4.1). Winter daily minimum air temperatures showed the most change since the beginning of record in 1873. The slopes of the linear models were significant ( $p < 0.05$ ) for the Annual, Summer, Fall and Winter means, and are shown along with a 95 % confidence interval in Figure 4.1. This average increase in temperature is consistent with the IPCC report on regional climate warming, which indicated an increase of 0.75-1.5 °C for eastern North America from 1990 - 2015 (Allen et al., 2018).

A LOESS curve with a span of 0.15 was applied to each temperature plot to aide in visualizing the variability and to reduce noise in temperature regime across the dataset (Figure 4.1). Annual temperature fluctuations (Figure 4.1a) across the dataset generally oscillate on a decadal basis. This could relate to the North Atlantic Oscillation (NAO), where positive NAO index years are correlated with above average temperatures in eastern North America (Durkee et al., 2008). For example, the high temperatures in the late 1990s and early 2000s observed in Figure 4.1a align with positive NAO index years from 1998 to 2000 identified by Durkee et al. (2008).

A  $\sim 1$  °C increase in average annual air temperature can influence lake temperature, stratification, period of ice overage and turn-over timing (Filazzola et al., 2020). Winter months demonstrated the most warming of the seasons plotted. A warming climate in the winter month generally decreases winter ice coverage. Summer and Fall increases in air temperature can additionally increase the overall ice-free water temperatures, which can improve the habitability of the water for cyanobacteria (Enache et al., 2011). A 2020 study of 122 temperate Northern

Hemisphere lakes over a period of 78 years showed that the number of years that the lakes were ice-free has become more frequent. Ice-free years are closely related to winter air temperatures and climate oscillations (Filazzola et al., 2020). Several of the lakes included in this study were in Maine, USA, which has similar climate patterns to Nova Scotia (MacLeod & Korycinska, 2019). Filazzola et al. (2020) also applied IPCC climate change scenarios to project the frequency of future ice-free events in the study lakes. Lakes are sensitive systems that are highly responsive to climate shifts and extremes (Filazzola et al., 2020), which has cascading consequences for both recreational and cultural activities as well as ecological response. Data for ice coverage periods in Mattatall and Angevine Lakes is not available, but future research could use observed winter air temperatures to estimate/predict ice coverage.



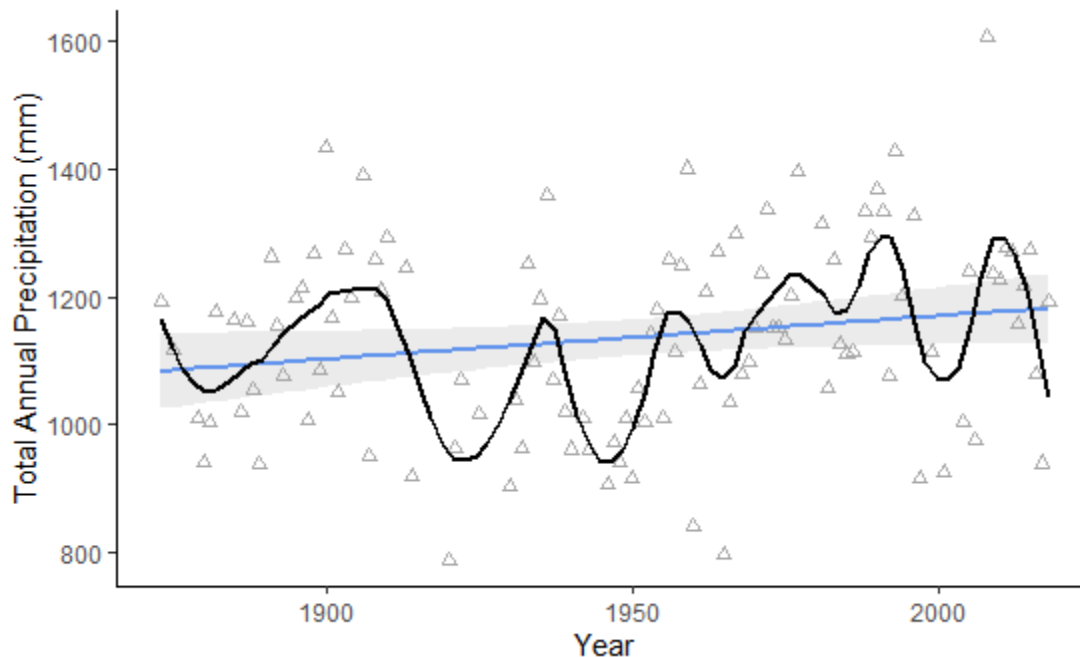


**Figure 4.1: Average minimum air temperatures for Annual (A), Summer (B), Fall (C) and Winter (D) from 1873 to 2019. Blue regression lines are accompanied by a 95% CI in grey. A LOESS curve with a span of 0.15 is shown in black. Each plot is labelled with the overall change in air temperature for that plot.**

#### 4.1.2 Total Annual Precipitation

A 148-year record of total annual precipitation is shown in Figure 4.2. Linear regression analysis was applied to determine the overall change in precipitation since the beginning of the record in 1873 to the end of record in 2019. Annual precipitation has not increased significantly across the record as indicated by the slope of the linear model not being significant.

A LOESS curve with a span of 0.15 was applied to the plot in Figure 4.2 to aide in visualizing variability and reduce noise in the precipitation regime across the dataset. Similar to the temperature data, precipitation appears to fluctuate on a decadal basis. This sinusoidal pattern of precipitation may be partly related to the NAO, where positive NAO index years are associated with increased precipitation (Durkee et al., 2008). Positive NAO index years occurred from 1988 to 1995 (Durkee et al., 2008), and these align well with higher precipitation values observed in Figure 4.2. However, periods of increased precipitation do not always align with the positive NAO index years identified by Durkee et al. (2008). For instance, precipitation actually decreases in northern NS in the 1998-2000 positive NAO index years (Durkee et al., 2008).



**Figure 4.2 Total annual precipitation from 1873 to 2019. A blue regression line is accompanied by a 95% CI in grey, this line was not significant. A LOESS curve with a span of 0.15 is shown in black.**

## 4.2 Lake Characteristics

Mattatall and Angevine Lakes are described and compared based on their morphometry, water chemistry, trophic state, and *in-situ* chemistry profiles.

### 4.2.1 Morphometry

Mattatall and Angevine Lakes are of a similar size and maximum depth (Table 4.1). They also have a similar flushing rate of slightly less than twice a year. Angevine Lake flushes 1.75 times per year, while Mattatall Lake flushes 1.99 times per year. Mattatall Lake contains three distinct basins, so a separate flushing rates were calculated for each basin according to the respective area draining into each respective basin. Basin 1 had the slowest flushing rate of 0.7 times per year (Table 4.1).

**Table 4.1: Lake morphological characteristics**

Parameter	Units	Mattatall	Angevine
Lake Surface	ha	118.6	151.2
Volume	10 <sup>6</sup> m <sup>3</sup>	4.34	6.34
Max Depth	m	11.0	14.6
Mean Flushing Rate	yr <sup>-1</sup>	Basin 1: 0.7 Basin 2: 3.2 Basin 3: 4.6	1.75

Mattatall and Angevine Lake differ in the number of distinct basins forming each lake. Angevine Lake has a singular elongated basin (Figure 3.2). In contrast, Mattatall Lake is a series of 3 basins, with the first (Basin 1) being the deepest. The surface area of the deep basin is small relative to the rest of the lake (Figure 3.2). The morphometry of these lakes influences the development of lake stratification in each lake uniquely. In Mattatall Lake, the volume of the hypolimnion is  $1.61 \times 10^5 \text{ m}^3$  relative to a lake volume of  $4.43 \times 10^6 \text{ m}^3$ ; therefore, hypolimnetic water occupies 3.63 % of the lake volume. These smaller deep basins with slow flushing rates tend to lead to the rapid development of anoxic conditions if depth is sufficient, as observed in many studies (James, 2017; Nürnberg et al., 2012; Paerl & Huisman, 2008; Vahtera et al., 2007). The volume of the hypolimnion in Angevine Lake is  $3.29 \times 10^5 \text{ m}^3$ , relative to a lake volume of  $6.34 \times 10^6 \text{ m}^3$ ; therefore, hypolimnetic water occupies 5.14 % of the lake volume. This is a larger

hypolimnion in contrast to Mattatall Lake. A larger hypolimnion with a swifter flushing rate (1.75 times per year) can result in prolonged oxic conditions during stratification.

#### 4.2.2 General Water Chemistry

A summary of water quality results for the 2018 and 2019 water sampling program at Mattatall and Angevine Lakes is presented in Table 4.2.

Mattatall Lake was circum-neutral with a mean pH of 6.8. Mean alkalinity, an indicator of the buffering capacity of the water, was 12 mg/L. Buffering capacity of lakes in Nova Scotia is highly dependent on the local geology. Lakes underlain by igneous and metamorphic bedrock have low buffering capacity, and typically have undetectable alkalinity (Underwood & Schwartz, 1990). Since Mattatall Lake overlies sedimentary units, and has detectable alkalinity, its buffering capacity would be considered moderate for Nova Scotia surface waters (Underwood & Schwartz, 1990). Mattatall Lake has soft water, with a mean hardness of 13.3 mg/L (< 60 mg/L is considered soft) and total calcium was 4467 µg/L. Other parameters of interest that would have an influence on light penetration include TOC which was 5 mg/L, and colour which was 23 TCU. Mattatall Lake would therefore be considered a clear to slightly coloured lake, where colour values ≤ 20 TCU are considered clear (Kerekes et al., 1990). In terms of nutrient concentrations, Mattatall Lake was classified as mesotrophic with respect to TP, with an average of 14 µg/L. The N:P ratio was 12, indicating the lake was not P deficient (Hecky et al., 1993). This N:P value should be interpreted with caution as only 2 samples for nitrate-nitrite (as N) were above the detection limit of 0.050 mg/L (Table 4.2). These data indicate that Mattatall is a low N system. This might have relevance as the HAB that was dominant in Mattatall Lake, *D. planctonicum*, is from a genus of cyanobacteria that are able to fix N from the atmosphere, giving them a competitive advantage (Kelly et al., 2021). Therefore, sufficient P was all that was necessary to support the *D. planctonicum* bloom.

Angevine Lake was circum-neutral with a mean pH of 6.8. Mean alkalinity was 9 mg/L, which like Mattatall Lake is considered moderate for Nova Scotia surface waters (Underwood & Schwartz, 1990). Angevine Lake has soft water, with a mean hardness of 8.3 mg/L and total calcium was 2300 µg/L. Total organic carbon was 6.4 mg/L, and colour was 30.6 TCU. This was slightly higher than Mattatall Lake, but Angevine Lake would still be considered clear/slightly coloured (Kerekes et al., 1990). In terms of nutrient concentrations, Angevine Lake was

classified as mesotrophic with respect to TP, with an average of 12 µg/L. The N:P ratio was 11, indicating the lake was not P deficient (Hecky et al., 1993). Like Mattatall Lake, this value should be interpreted with caution because only 1 sample from Angevine Lake was above the nitrate-nitrite (as N) detection limit of 0.050 mg/L (Table 4.2). However, it can be generally inferred that Angevine Lake is a low N system.

In summary, Mattatall Lake and Angevine Lake broadly share the following attributes:

- Neutral pH
- Soft water
- Clear to slightly coloured water, low TOC
- Mesotrophic TP concentrations
- Low N concentrations

#### 4.2.3 *Trophic status*

The values of the parameters used to classify the trophic state (including TP, chl-a, and SD) of Mattatall Lake and Angevine Lake are summarized in Table 4.3. The trophic state as determined by these values is then summarized in Table 4.4 based on threshold ranges established by CCME (2004) and Vollenweider and Kerekes (1982).

Based on the evaluations in Table 4.4, both Mattatall and Angevine Lakes were determined to be oligo-mesotrophic. Total phosphorus in both lakes indicate that they are mesotrophic. Chlorophyll-a in Mattatall Lake indicates mesotrophic conditions while in Angevine Lake oligotrophic conditions are inferred. Secchi disk depth in both lakes were generally indicative of oligotrophic conditions.

Oligo-mesotrophic lakes are generally considered low risk for HAB events (Johnston et al., 2021). Therefore, Angevine Lake demonstrates seasonal patterns that would be expected of an oligo-mesotrophic lake, i.e. seasonal fluctuations in clarity and nutrient levels, some increased biological productivity in the late summer, but no HABs. For the time that Mattatall Lake has been observed (2017 – Present) it has followed the same pattern as Angevine Lake, with the exception of slightly more biological activity. Prior to 2017, the three HAB events that occurred were atypical of an oligo-mesotrophic lake and indicate that more complex processes are likely operating in this lake that are not captured within general trophic state classification.

**Table 4.2: Summary of water quality parameters and their reporting detection limits (RDL) measured in Mattatall Lake and Angevine Lake.**

Parameter	Units	RDL	Mattatall Lake				Angevine Lake			
			Min	Max	Mean	n	Min	Max	Mean	n
<b>pH</b>	pH	N/A	6.6	7.2	6.8	6	6.6	7.1	6.8	7
<b>Total Alkalinity (as CaCO<sub>3</sub>)</b>	mg L <sup>-1</sup>	5	12	12	12	3	8	10	9	5
<b>Conductivity</b>	uS cm <sup>-1</sup>	1.0	43.0	49.0	46.0	3	32.0	42.0	38.0	5
<b>Turbidity</b>	NTU	0.10	1.10	1.20	1.13	3	1.20	2.60	1.84	5
<b>Colour</b>	TCU	5.0	17.0	27.0	23.0	3	16.0	47.0	30.8	5
<b>Calculated TDS</b>	mg L <sup>-1</sup>	1.0	26.0	27.0	26.3	3	19.0	22.0	20.6	5
<b>Hardness (as CaCO<sub>3</sub>)</b>	mg L <sup>-1</sup>	1.0	13.0	14.0	13.3	3	7.8	9.0	8.3	5
<b>Total Sodium</b>	ug L <sup>-1</sup>	100	4000	4400	4167	3	3800	4400	4160	5
<b>Total Potassium</b>	ug L <sup>-1</sup>	100	430	490	453	3	440	480	460	5
<b>Total Magnesium</b>	ug L <sup>-1</sup>	100	500	550	520	3	580	670	614	5
<b>Total Calcium</b>	ug L <sup>-1</sup>	100	4300	4600	4467	3	2200	2500	2300	5
<b>Dissolved Chloride</b>	mg L <sup>-1</sup>	1.0	6.9	7.7	7.2	3	5.2	6.8	5.8	5
<b>Reactive Silica</b>	mg L <sup>-1</sup>	0.5	1.1	2.0	1.6	3	0.8	2.5	1.7	5
<b>Nitrate-Nitrite (as N)</b>	mg L <sup>-1</sup>	0.050	0.072	0.078	0.075	2	0.058	0.058	<0.058	1
<b>Total Phosphorus</b>	µg L <sup>-1</sup>	4	11	15	14	6	10	14	12	7
<b>Total Organic Carbon</b>	mg L <sup>-1</sup>	0.1	4.8	5.1	5.0	3	5.4	6.9	6.4	5
<b>Total Aluminum (Al)</b>	ug L <sup>-1</sup>	5.0	22.0	58.0	38.7	3	40.0	150.0	86.8	5
<b>Total Barium (Ba)</b>	ug L <sup>-1</sup>	1.0	31.0	33.0	32.0	3	22.0	26.0	23.8	5
<b>Total Cadmium (Cd)</b>	ug L <sup>-1</sup>	0.010	0.012	0.012	<0.012	3	0.110	0.110	<0.11	1
<b>Total Chromium (Cr)</b>	ug L <sup>-1</sup>	1.0	1.1	1.1	<1.1	3	1.1	2.1	<1.6	2
<b>Total Copper (Cu)</b>	ug L <sup>-1</sup>	2.0	0.6	1.7	1.0	3	0.6	0.8	<0.71	3
<b>Total Iron (Fe)</b>	ug L <sup>-1</sup>	50	91	110	100	3	110	210	156	5
<b>Total Manganese (Mn)</b>	ug L <sup>-1</sup>	2.0	20.0	35.0	25.3	3	34.0	120.0	56.0	5
<b>Total Strontium (Sr)</b>	ug L <sup>-1</sup>	2.0	12.0	14.0	13.0	3	11.0	13.0	11.6	5

**Table 4.3: Parameter values for trophic state evaluation for Mattatall Lake and Angevine Lake. Mean values are presented as the mean  $\pm$  standard deviation.**

Lake		Anoxic zone thickness (m)	pH	Mean colour (TCU)	Mean TP ( $\mu\text{g/L}$ )	Mean Chl-a ( $\mu\text{g/L}$ ) <sup>b</sup>	Max Chl-a ( $\mu\text{g/L}$ ) <sup>b</sup>	Mean SDT (m)	Max SDT (m)
Mattatall	Basin 1	1	6.8	23 $\pm$ 5	14 $\pm$ 1.4	3.3 $\pm$ 1.3	5	3.4 $\pm$ 0.3	3.8
	Basin 2	0	7	28 $\pm$ 9	14 $\pm$ 1.8	4.2 $\pm$ 2.2	8.2	3.4 $\pm$ 0.3	3.7
	Basin 3	1.3	7	27 $\pm$ 8	14 $\pm$ 1.9	3 $\pm$ 0.98	4.5	3.6 $\pm$ 0.4	4
Angevine <sup>a</sup>		3.5	6.8	31 $\pm$ 12	12 $\pm$ 1.8	2.3 $\pm$ 1.1	3.9	3.2 $\pm$ 0.7	4.3

<sup>a</sup>Combined data from the 2018 and 2019 open water seasons

<sup>b</sup>Whole water column arithmetic mean

**Table 4.4: Trophic state classification of Mattatall and Angevine Lakes, where M = mesotrophic and O = oligotrophic.**

Lake		Total Phosphorous	Chlorophyll-a		Secchi Depth	
			Mean	Max	Mean	Max
Mattatall	Basin 1	M	M	O	O	O
	Basin 2	M	M	M	O	O
	Basin 3	M	M	O	O	O
Angevine		M	O	O	M	O

#### 4.2.4 In situ *Water Chemistry Profiles*

*In-situ* water column profile data was taken from Basin 1 (the deepest basin) in Mattatall Lake (Figure 3.1). Water temperature profiles for Mattatall Lake are summarized in Figure 4.3. Mattatall Lake is completely mixed in the spring and fall but becomes stratified in the summer with the thermocline starting at 3 m depth and a hypolimnion from 6 m depth to bottom (Figure 4.3).

Water temperature profiles at Angevine Lake are also summarized in Figure 4.3. Angevine Lake was well mixed in the spring and fall. In the summer, the lake became stratified with the thermocline starting at 4 m depth and a hypolimnion from 8 m depth to bottom (Figure 4.3). Water temperature appears to be overall cooler in Angevine Lake compared to Mattatall Lake in the spring. This is due to the spring sampling events taking place on different dates, Angevine Lake was sampled in April 2018, while Mattatall was sampled in May 2019.

The DO profiles at Mattatall Lake follow a similar pattern as the temperature data. Dissolved oxygen is near 100% saturation in the spring and fall when the lake is mixed. In the summer, the DO of the hypolimnion depleted to 0 % saturation (Figure 4.4). The profundal zone of Basin 1 in Mattatall Lake is relatively small and deep, and water flow through the basin is constricted. The stagnation of the hypolimnetic water is further exacerbated when the colder temperatures increase water density, preventing mixing with overlying water layers. Under these conditions any available oxygen is consumed by the degradation of organic matter (phytoplankton, humic acid molecules, etc.) within the lake sediments (Nürnberg, 1995).

The DO profiles from the spring and fall at Angevine Lake showed that the lake was at 100 % DO saturation throughout the water column, indicating the water was both well mixed and oxygenated (Figure 4.4). In the summer during stratification, the DO was at 100 % saturation in the epilimnion. The hypolimnion of Angevine Lake became hypoxic and approached 0 % saturation at the sediment-water interface. The deep basin of Angevine is large and elongated relative to the rest of the lake. While the hypolimnetic water is denser and did not likely mix with the water above, it has a greater volume relative to the surface area of lake sediment and it will take longer for the oxygen to be consumed by decomposers within the lake sediment. This contrasts with Mattatall Lake where 0 % DO was achieved through the entirety of the hypolimnion by the same sampling date (Figure 4.4; summer).



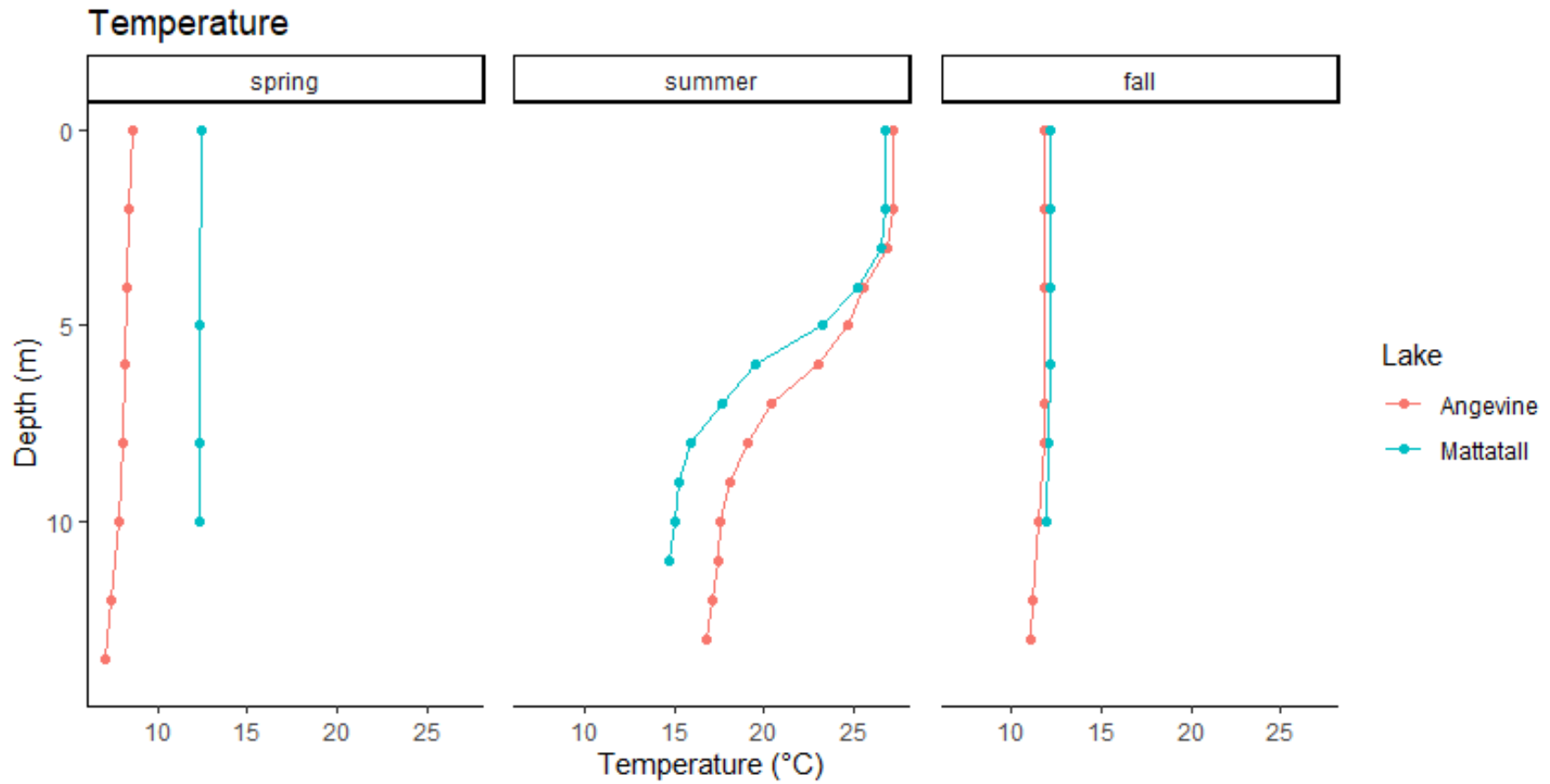


Figure 4.3: Water temperature profiles for Mattatall and Angevine Lakes.

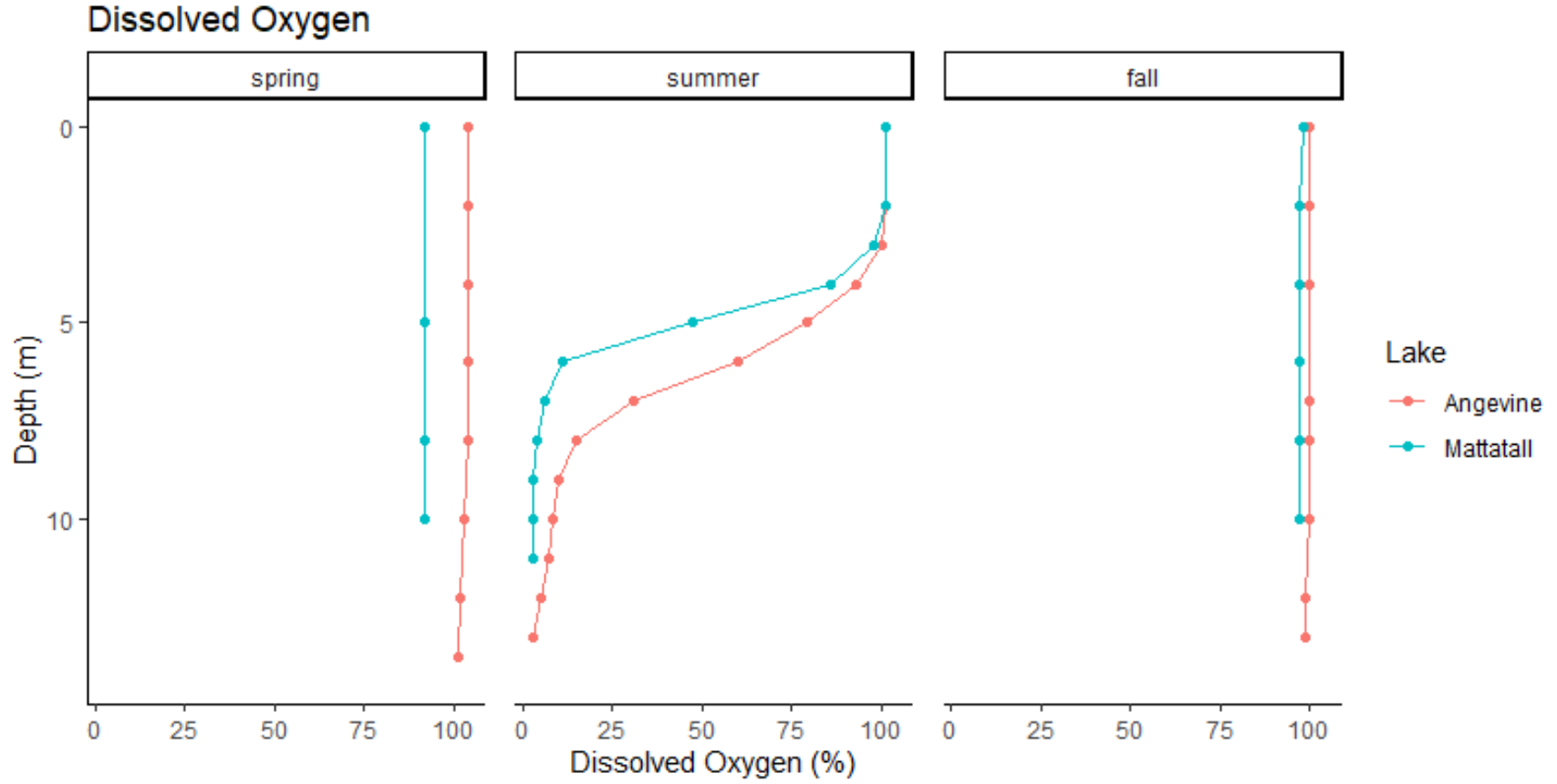


Figure 4.4: Dissolved oxygen profiles for Mattatall and Angevine Lakes.

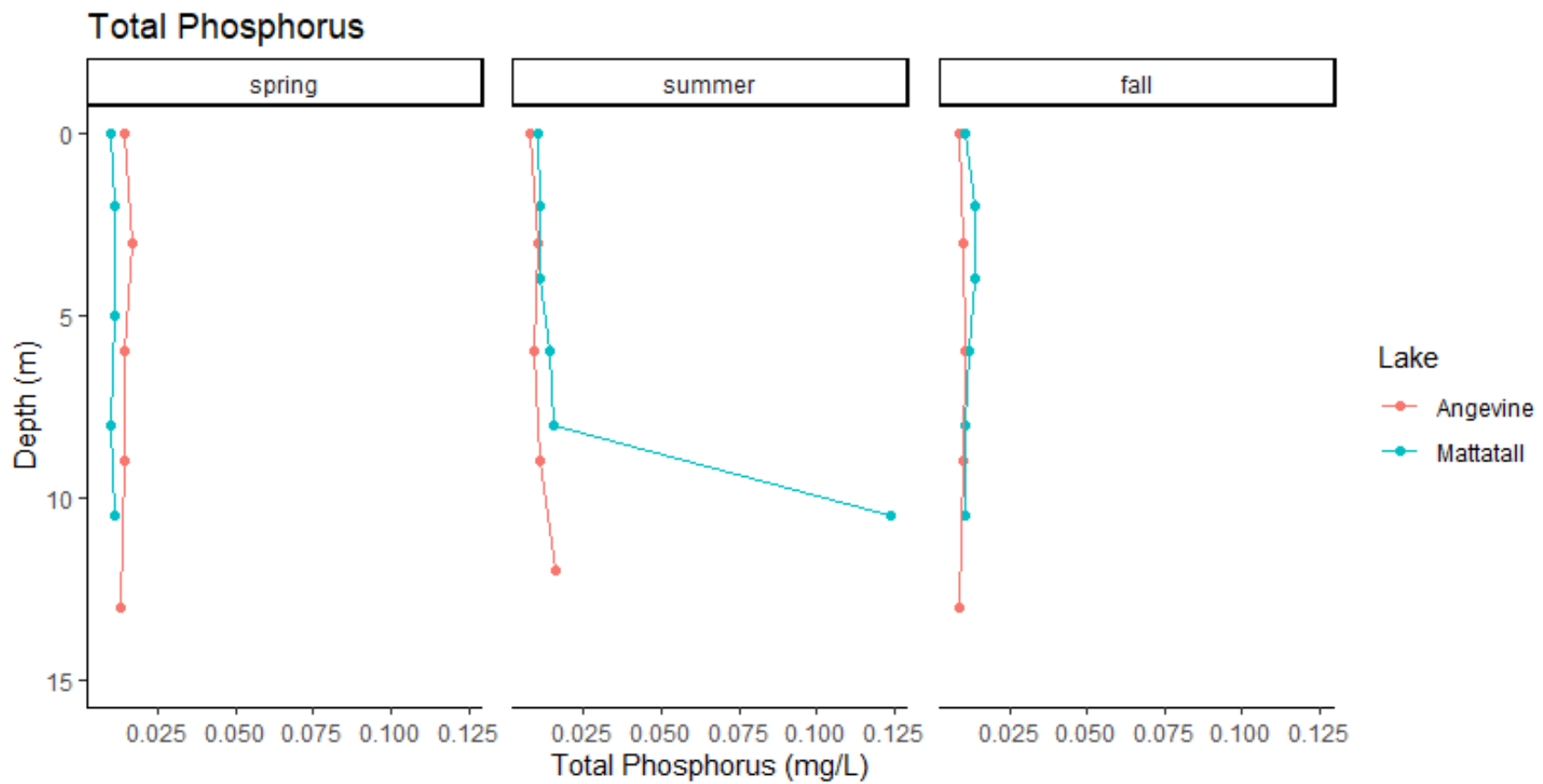
The TP in Mattatall Lake was observed to be  $< 0.02$  mg/L throughout the water column in the spring and fall when that lake was mixed (Figure 4.5). In the summer, the TP was  $< 0.02$  mg/L except for the bottom sample collected above the sediment/water interface where TP increased to  $0.125$  mg/L (Figure 4.5). The SRP was below the detection limit of  $0.001$  mg/L for the spring and fall through the water column. In the summer, the SRP was below detection in the epilimnion and metalimnion, followed by a detectable concentration of  $0.100$  mg/L at the bottom of the water column (Figure 4.6).

The presence of higher concentrations of TP and SRP at the bottom of the water column is frequently observed in lakes where the hypolimnion becomes anoxic during summer stratification (Nürnberg et al., 2012; Tammeorg et al., 2017). The shift in redox conditions at the sediment water interface has been attributed to the release of P back into the water column from where it was formerly bound within the lake sediment. Gächter & Müller (2003) found that sediment P retention is also related to the availability of reactive Fe(II),  $S^{2-}$  and  $PO_4^{3-}$ . The ratios of these elements are further driven by the nature of the organic matter and particulate iron in the lake's sediment (Gächter & Müller, 2003). In summary, lakes with high iron but low sulfate will have a greater capacity to permanently retain P regardless of redox conditions, while increased sulfide production could lead to more P release (Gächter & Müller, 2003). This more nuanced understanding of P release processes is important to consider in terms of whether artificial oxidation would be an effective method to control internal P loading in lakes (Gächter & Müller, 2003; Tammeorg et al., 2017). For the purposes of this study, it can be surmised that anoxic stratification is occurring at Mattatall Lake and SRP is effectively being released. To summarize, the mechanism by which this P release is occurring is likely related to the redox conditions, but there could be other important geochemical processes influencing the release of P that are beyond the scope of current understanding at Mattatall Lake.

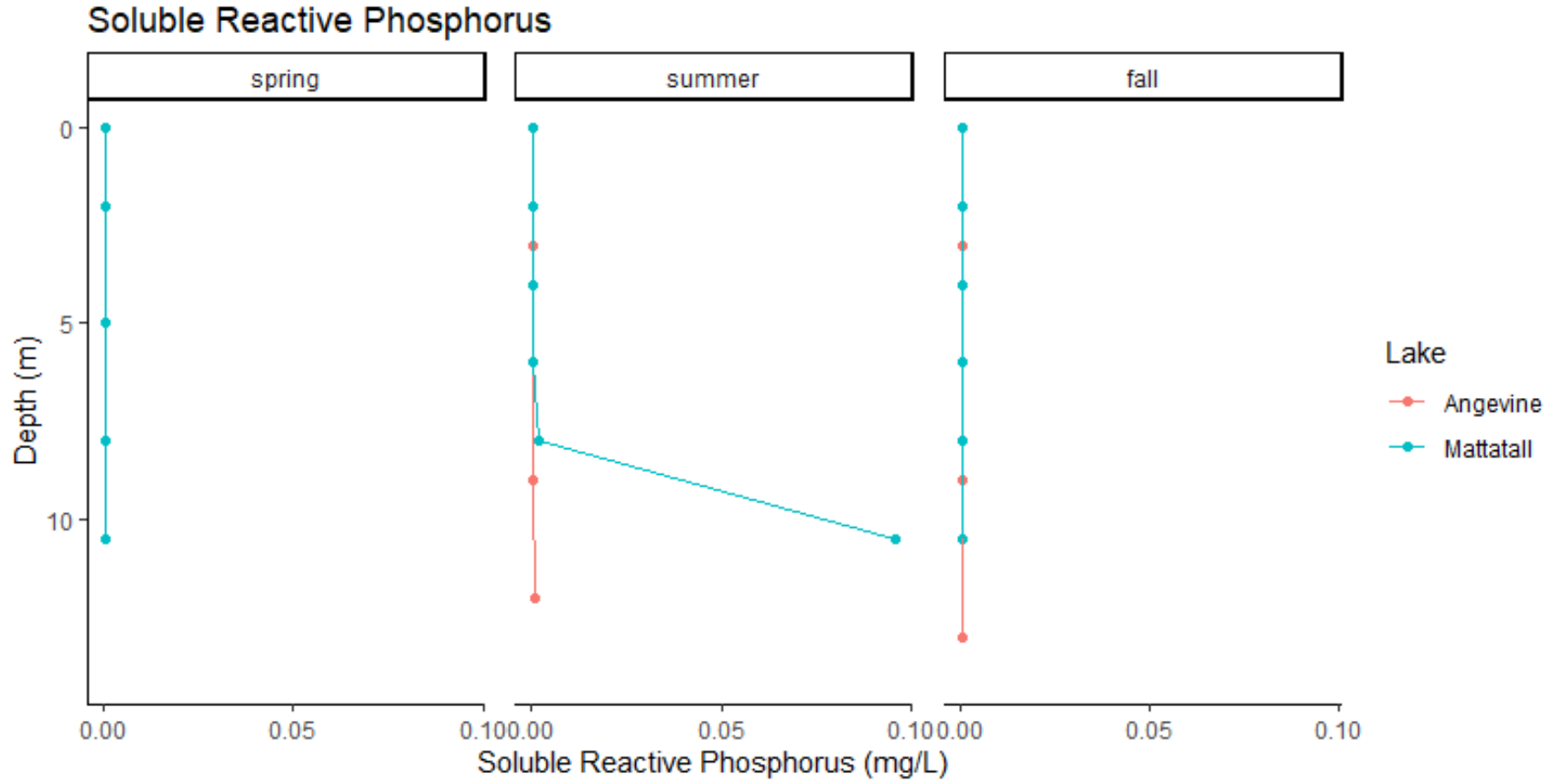
The TP in Angevine Lake was observed to be between  $0.01$  and  $0.015$  mg/L in the spring, summer, and fall (Figure 4.5). There was some variability of TP concentrations throughout the water column in the profiles of each season. The summer TP profile (Figure 4.5) of Angevine Lake showed an increase in TP concentration at the bottom of the profile, which could indicate some P resuspension. However, the difference between the bottom sample, and samples from the rest of the water column was small ( $+ 0.005$  mg/L). There are no profiles for SRP in Angevine

Lake because it was below the detection limit of 0.001 mg/L in the spring, summer and fall throughout the water column.

Since SRP does not occur at detectable concentrations in Angevine Lake, it is likely that this lake either (a) does not become anoxic, or is not anoxic long enough for SRP to be released from the lake sediment, and/or (b) the geochemistry of Angevine Lakes sediments is better suited to retaining P. In either case this is an important point of contrast between limnological conditions in Mattatall Lake and Angevine Lake. Angevine Lake demonstrates conditions that are typical in a single, large basin lake where stratification leads to oxygen depletion, but not to the extent that SRP is being resuspended from the lake sediment (Butcher et al., 2015). In contrast, Mattatall Lake has a low volume, constricted, deep basin where anoxia can occur earlier in the summer during stratification such that SRP can be effectively resuspended. While sediment geochemistry has an intrinsic role in this process, it is also controlled largely by basin morphometry.



**Figure 4.5: Total phosphorus profiles for Mattatall and Angevine Lakes.**



**Figure 4.6: Soluble reactive phosphorus profiles for Mattatall and Angevine Lakes.**

Chlorophyll-a was present in concentrations of 4-5  $\mu\text{g/L}$  through the water column of Mattatall Lake in the spring and fall, when the water was mixed (Figure 4.7). During summer stratification, chl-a concentrations in the epilimnion were 3.4  $\mu\text{g/L}$  which were lower than in the spring and fall. These values decreased to  $< 2 \mu\text{g/L}$  in the hypolimnion and increased to  $\sim 4 \mu\text{g/L}$  in the lake bottom sample (Figure 4.7).

Photosynthetic organisms have access to light throughout most of Mattatall Lake's water column because the depth of the euphotic zone is on average 8.5 m, with a recorded maximum depth of 9.5 m (Table 4.3). The chl-a profile in the summer can therefore be explained as a grouping of photosynthetic taxa in the top 5 m of the water column which are likely prevented from migrating deeper due to the thermocline, or perhaps the buoyancy of the species that were present (Regel et al., 2004). The time of day of sampling can also impact where the taxa are concentrated (Regel et al., 2004). A decrease in biological activity in the thermocline usually follows. In the hypolimnion, an increase in photosynthetic taxa activity occurred at the bottom of the lake as many species of benthic algae are adapted to the low light conditions (Cantonati & Lowe, 2014).

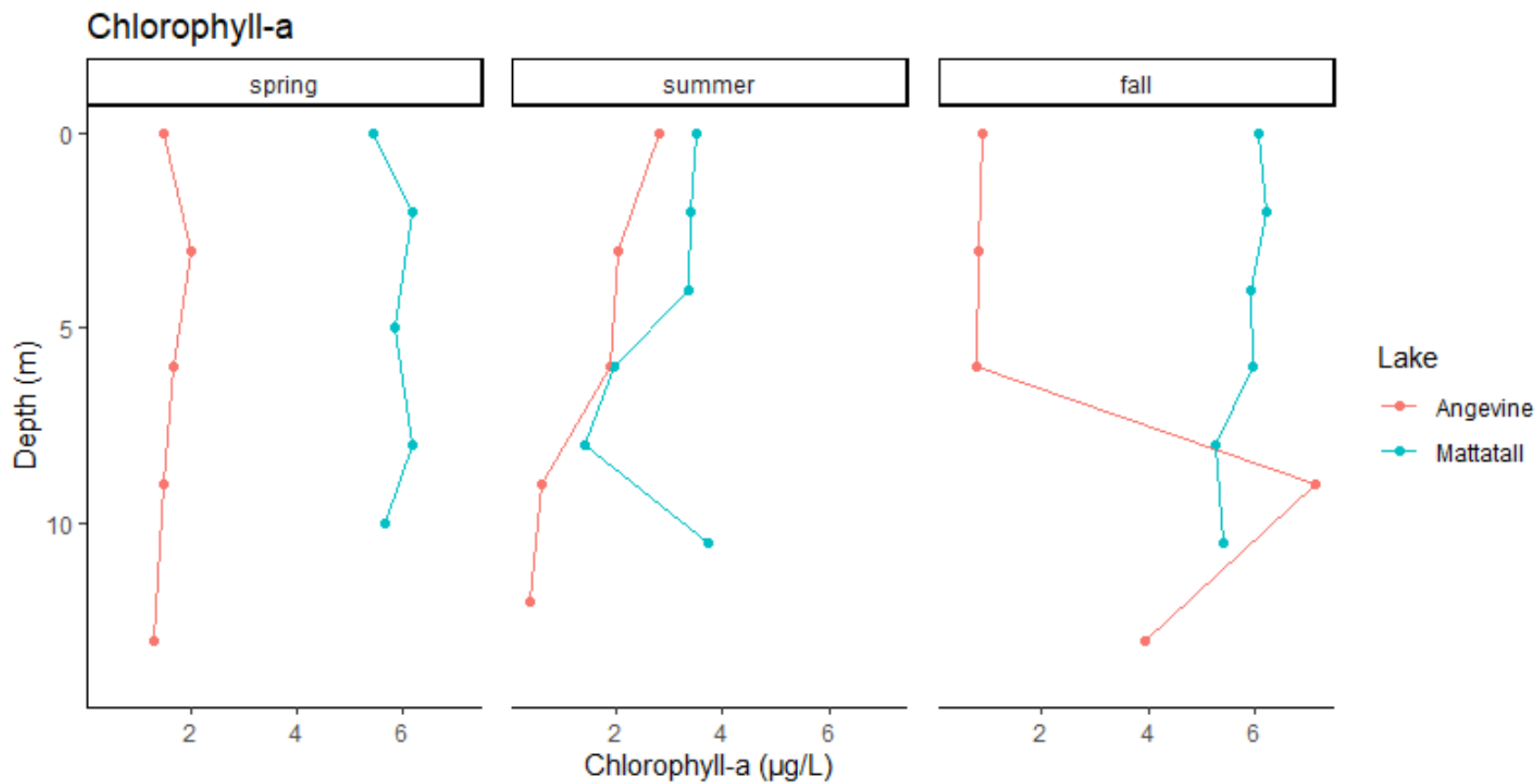
In the spring and fall Mattatall Lake is mixed, and since light is available throughout most of the water column, the photosynthetic taxa are distributed uniformly throughout the water column. There is a higher concentration of chl-a in the spring compared to the summer likely due to enhanced nutrient availability from spring thaw and runoff bringing an influx of nutrients into the lake. Similarly, in the fall, the lake mixes and the photosynthetic taxa once again are distributed uniformly throughout most of the water column. However, chl-a concentrations increase in this case because the fall turnover distributes the nutrients concentrated in the hypolimnion during stratification (namely the SRP), to the rest of the water column. Given that two of the observed algae blooms in Mattatall Lake occurred in the fall and originated in Basin 1, it is this pulse of bioavailable SRP that occurs during the fall turn over that likely increases the HAB vulnerability of Mattatall Lake.

Chlorophyll-a during the spring in Angevine Lake was mostly consistent throughout the water column at  $\leq 2 \mu\text{g/L}$  (Figure 4.7). During summer stratification, chl-a concentrations increased to  $\sim 3 \mu\text{g/L}$  at the water surface, and steadily decreased with depth with the lowest concentration observed in the lake bottom sample of ( $< 1 \mu\text{g/L}$ ). In the fall, chl-a was lowest at

the water surface at  $\sim 1 \mu\text{g/L}$ , then increased to  $> 6 \mu\text{g/L}$  at approximately 8 m depth, then decreased to  $4 \mu\text{g/L}$  at the lake bottom sample (Figure 4.7).

Photosynthetic organisms in Angevine Lake have access to light throughout most of the water column. On average the euphotic zone extends to 8 m, with a recorded maximum of 10.8 m (Table 4.3). Where the lake has a maximum depth of 14.6 m (Table 4.1), a proportion of the water column below 10 m would be more light-limited. This is evident in the summer chl-a profile where there is no evidence of benthic algal activity as was observed in Mattatall Lake. The fall profile of Angevine Lake shows evidence of a concentrations of photosynthetic taxa at 8 m depth. This might be attributed to the buoyancy of the taxa that were present, or the time of sampling. Some phytoplankton are known to migrate up and down the water column to optimize light intensity (Regel et al., 2004; Whittington et al., 2000). Spring and fall chl-a concentrations are notably lower overall in Angevine Lake when compared to Mattatall Lake. This could be due to the differing sampling dates. Chlorophyll-a was also higher concentrated in Mattatall Lake compared to Angevine Lake in the fall (Figure 4.7). This could be attributed to Angevine Lake having limited resuspension of P, especially SRP which was not detected. This provides much less opportunity for biological uptake and proliferation in Angevine Lake.





**Figure 4.7: Chlorophyll-a profiles in Mattatall and Angevine Lakes.**

### 4.3 Landscape change

Landscape change (i.e. forest removal, agricultural activities, residential and road infrastructure development) has a vital influence on lake characteristics and water quality. As a near universal solvent, the properties and characteristics of the lake water are dependent on the substances dissolved into the water during its transmission through the watershed. Moreover, watershed landscape can influence the temperature, volume and velocity of water movement into the lake system, windshear over the lake surface and sediment accumulation and quality at the lake bottom. These have a cascade of impacts on lake functions and biological activity.

#### 4.3.1 Road and Residential Infrastructure Development

Development in the Mattatall and Angevine Lake watersheds in terms of road and land clearing likely began in the early 1800s. While settlement by Mi'kmaq and Acadians existed prior to this time in the region, it was not until 1820 that population and land development began to expand in response to growth of the shipbuilding industry in nearby Tatamagouche (Milton, 2015). Records of exact periods of land clearing in the watersheds were not available, but the estimated time of the early 1800s was corroborated by paleolimnological evidence which is discussed further in section 4.4.

Landsat Imagery captured as early as 1985 indicate that by this time unpaved roads were present in both watersheds, and residential development along the shorelines was underway. Residential development has continued in both watersheds until present day. Mattatall Lake has a total of about 117 residences existing in the watershed at present as estimated with satellite imagery. Angevine Lake has an estimated 52 residences within its watershed.

A P source characterization study for Mattatall Lake was conducted in 2017 using an adaptation of the Nova Scotia Phosphorus Loading Model (CWRS, 2017). As part of the study, a detailed spatial analysis of land use types was conducted for the Mattatall Lake watershed for 1985 and 2016, the period in which the most significant landscape change has occurred in terms of residential developments and deforestation. The results of this study are summarized in Table 4.5. An estimated 17.6 ha of the 895 ha watershed has been developed for residential use (CWRS, 2017). An on-site waste-water survey was conducted, and of the 47 respondents, 12 were permanent residents, while 35 were seasonal (CWRS, 2017).

**Table 4.5: Land use types for the Mattatall Lake watershed in 1985 versus 2016 from CWRS (2017). Land use categories totals are expressed as a value followed by the percent cover in parentheses.**

Input	Year	Units	Basin 1	Basin 2	Basin 3	Total
Drainage Area (incl. lake area)	-	Ha	162	568	284	1 014
Drainage Area (excl. lake area)	-	Ha	129	526	240	895
Land use categories						
Roads	-	Ha	4.3	12	6.4	22 (2.5 %)
Residential	1985	Ha	3.0	2.1	0.0	5.1 (0.5 %)
Development	2016	Ha	6.0	7.5	4.1	18 (2.0 %)
Deforested	1985	Ha	0.0	0.0	9.8	9.8 (1.1 %)
	2016	Ha	0.0	42.0	33	75 (8.4 %)
Forested	1985	Ha	121	513	224	858 (95.9 %)
	2016	Ha	118	465	197	780 (87.2 %)

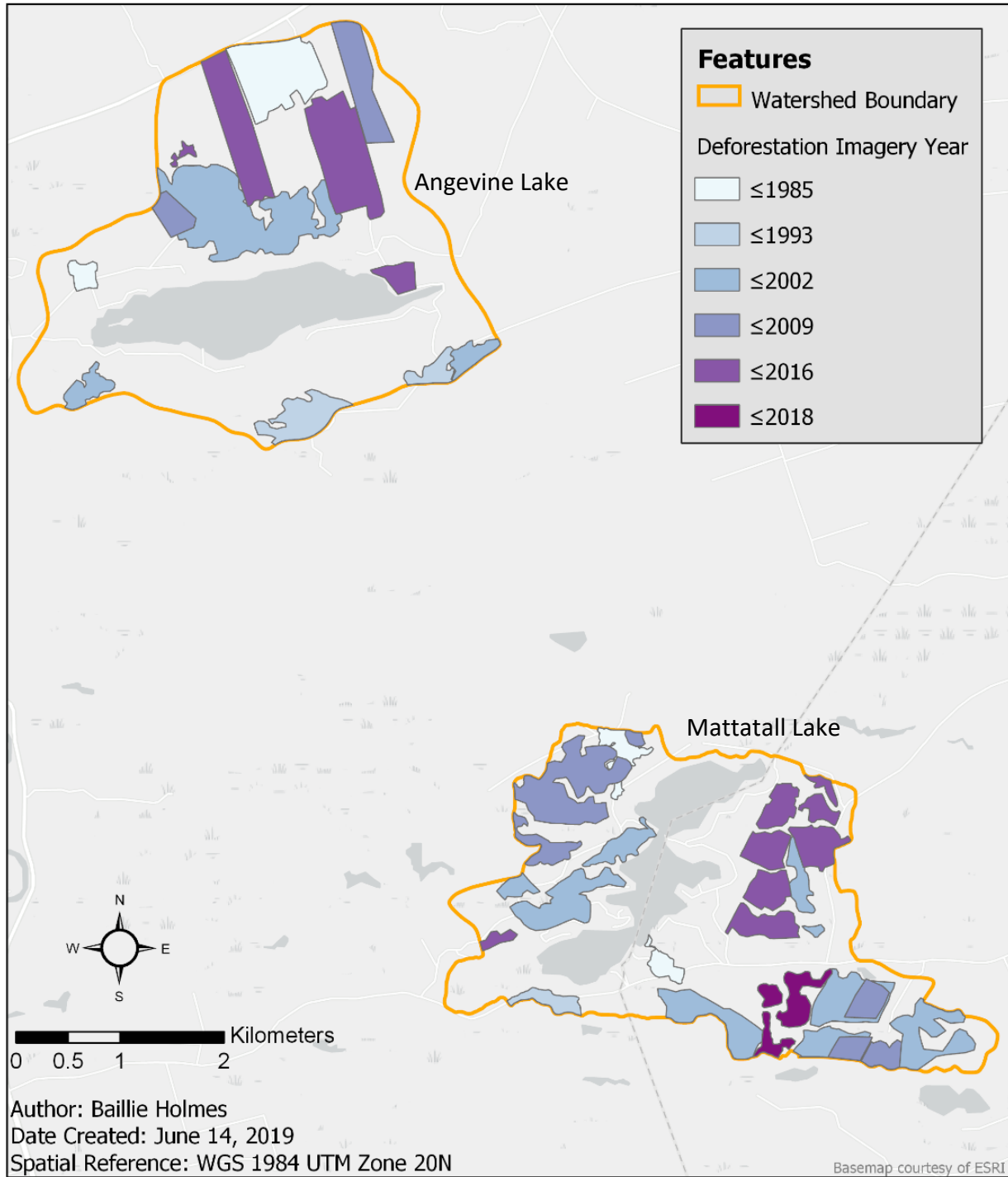
#### 4.3.2 Forest Removal Activities

Additional landscape change analysis was conducted to better understand forest removal activities since 1985 in both Mattatall and Angevine Lakes' watersheds. Regions of deforestation in the Mattatall and Angevine watersheds in 1985, 1993, 2002, 2009, 2016 and 2018 air photos are summarized in Figure 4.8. Polygons delineating clearance from different years were found to sometimes overlap, indicating that deforestation had happened multiple times in these regions. The most notable instance of this recurring deforestation is in the south-east region on the Mattatall Lake watershed (Figure 4.8).

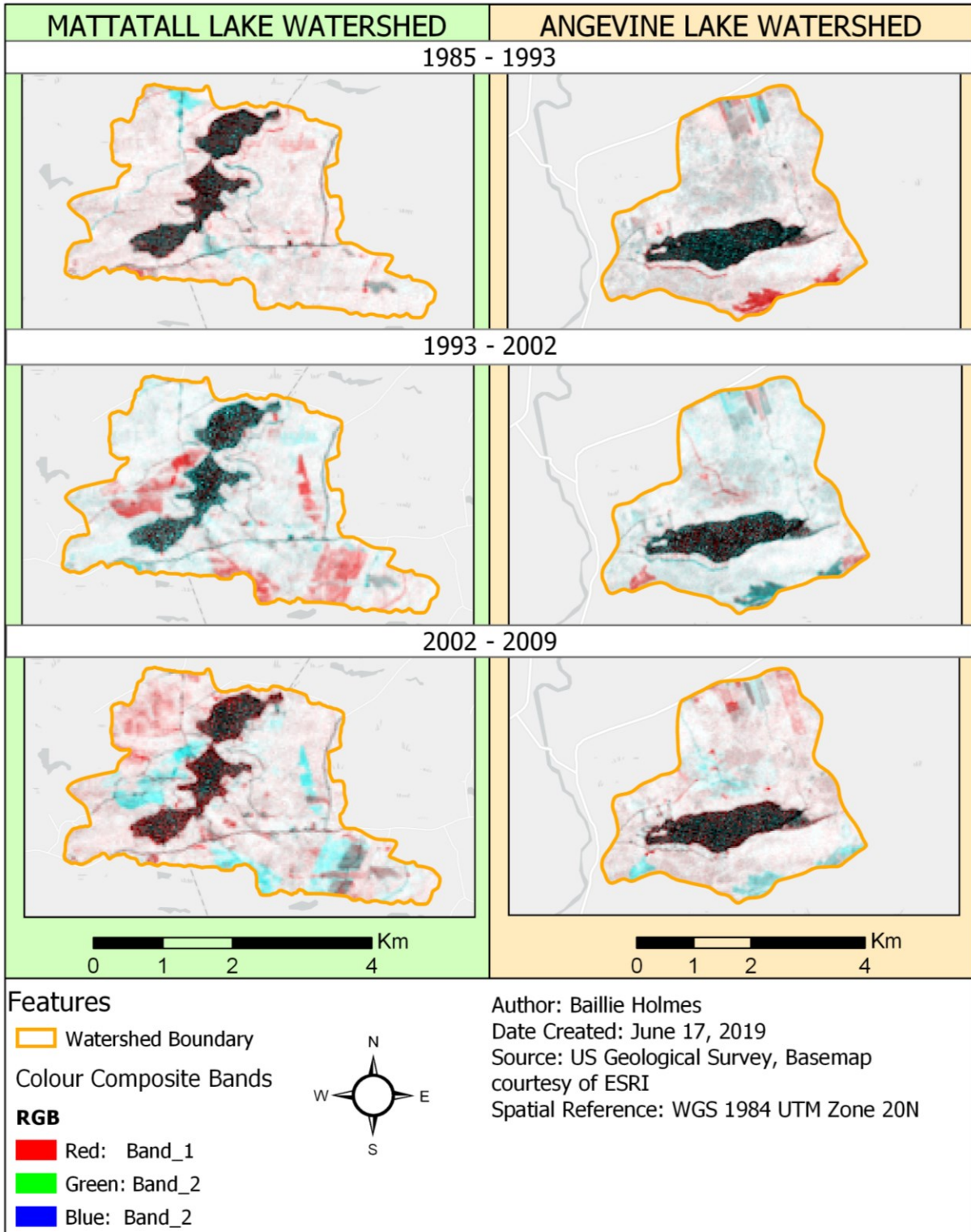
Normalized Difference Vegetation Index composite band images depicting changes in forest cover between study images are presented in Figure 4.9 and 4.10. In all colour composite images, areas that are red represent regions where NDVI values decreased from the first image to the second. In contrast, areas that are blue represent regions where NDVI values increased from the first image to the second. Areas that appear grey, or dull red/blue are where no change or very small change has occurred and may be disregarded.

There were considerable red (deforested) regions for every study year pair in Mattatall Lake, with most red zoning in the 1993 – 2002 composite (Figure 4.9). The Angevine Lake

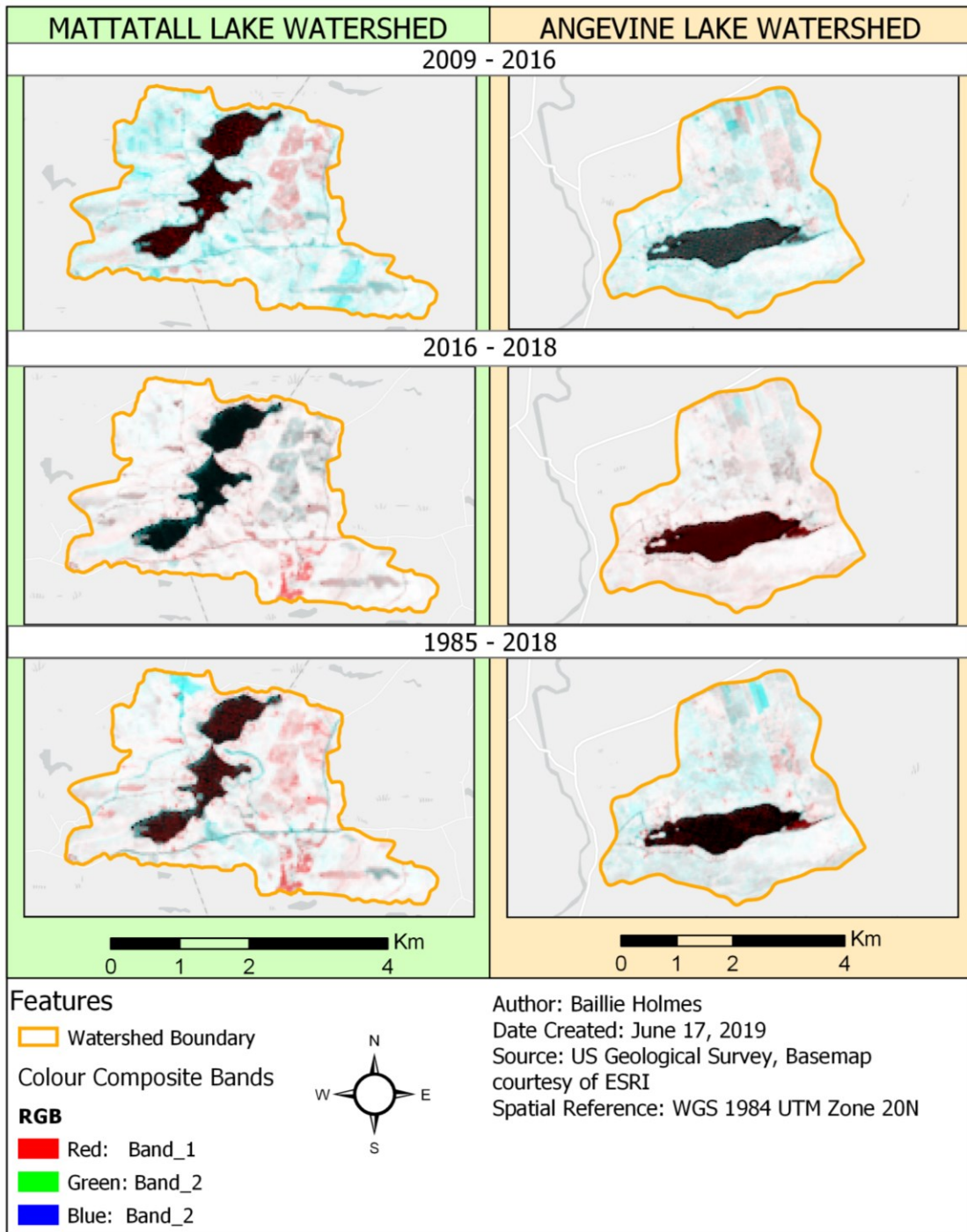
watershed had considerably less red zones (Figure 4.9). A composite was developed using the 1985 and 2018 NDVI values (Figure 4.10). This final composite revealed more red zoning and therefore overall NDVI depletion in the Mattatall Lake watershed since 1985. The Angevine Lake watershed appeared mostly blue, signalling NDVI improvement since 1985.



**Figure 4.8: Areas of deforestation in the Mattatall Lake and Angevine Lake watersheds from 1985 to 2018. Delineated from USGS Landsat Imagery.**



**Figure 4.9: Composite band images of Mattatall and Angevine Lake watersheds, where Band\_2 is the first (earlier) study image, and Band\_1 is the second (later) study image.**



**Figure 4.10: Continuation of composite band images of Mattatall and Angevine Lake watersheds, where Band\_2 is the first (earlier) study image, and Band\_1 is the second (later) study image.**

The approximate areas of deforestation for each of the study year pairs in Figures 4.9 and 4.10 were measured. In the 33-year study period, it was determined that the average percentage of deforestation in the Mattatall Lake watershed for each image pairing was  $7 \pm 3$  %, with a minimum of 2% in 2016 – 2018 and maximum of 13% in 1993 – 2002 (Table 4.5). The total cumulative disturbance footprint in Mattatall Lakes watershed was 403 ha, or 45 % of the watershed area. In the Angevine Lake watershed, the average percentage of deforestation for each image pairing was  $3 \pm 2$  %, with a minimum of 0.2 % in 2016 – 2018 and maximum of 6 % in 2009 – 2016 (Table 4.6). The total cumulative disturbance footprint in Angevine Lakes watershed was 185 ha, or 19 % of the watershed area. From a cumulative impact perspective, Angevine Lake has a comparatively lower disturbance footprint compared to Mattatall Lake.

**Table 4.6: Approximate areas of deforestation detected from Landsat imagery in the Mattatall Lake watershed. Areas were converted from  $30 \times 30$  m cell counts to hectares (ha).**

Imagery Year 1	Imagery Year 2	Deforested (ha)	Forested (ha)	Deforested (%)
1985	1993	27	866	3
1993	2002	115	777	13
2002	2009	80	812	9
2009	2016	92	801	10
2016	2018	22	870	2
1985	2018	67	825	8

**Table 4.7: Approximate areas of deforestation detected from Landsat imagery in the Angevine Lake watershed. Areas were converted from  $30 \times 30$  m cell counts to hectares (ha).**

Imagery Year 1	Imagery Year 2	Deforested (ha)	Forested (ha)	Deforested (%)
1985	1993	46	951	5
1993	2002	26	971	3
2002	2009	44	953	4
2009	2016	55	942	6
2016	2018	2	995	0.2
1985	2018	12	985	1



The Angevine Lake watershed has experienced less deforestation than the Mattatall Lake watershed in the past 33 years. While Mattatall Lake watershed was continually deforested in various locations, Angevine Lake watershed had longer forest recovery periods following cuts that occurred between 1985 and 1993. Deforestation at Angevine Lake since this time appears to be related to agricultural activity. The land appears to be vegetated and therefore the forest loss is not well captured by NDVI values. The Mattatall Lake watershed underwent greater deforestation related to clear cutting, and less related to agriculture.

Deforestation is a leading cause of soil erosion and nutrient export (Mrdjen, 2018; Paerl, 2014; Schindler et al., 2008). In the Mattatall Lake watershed, deforestation would increase the export of clastic material into the lake system, and therefore into the lake sediments. Nutrients such as P and N could be transported along with this material if these elements are present in the soils/parent rock that is being eroded. These nutrients would be in mineral forms and not necessarily available to biological agents.

Both Angevine and Mattatall Lake watersheds are underlain by Late Carboniferous Pictou-Stellarton Group sedimentary bedrock (NSDNR, 2006). These bedrock groups are comprised of sandstone, shale, conglomerate and minor limestone (NSDNR, 2006). In Nova Scotia, sedimentary bedrock units generally export more P than igneous or metamorphic bedrock units (CWRS, 2017). The soils in the Mattatall and Angevine Lake watersheds are dominated by the Queens, Debert and Kingsville soil groups, which are comprised of sandy clay loam, sandy loam, and sandy loam to sandy clay loam, respectively (Webb et al., 1991; Nowland and MacDougall, 1973). Drainage is imperfect to poor for most soils in both watersheds. Soils are underlain by compact till derived from shale and sandstone with < 20 % gravel. Mattatall Lake watershed has a few small areas of peat soils associated with bog wetland (Nowland and MacDougall, 1973).

The P export modelling conducted by CWRS in 2017 considered bedrock, soil, land clearing, on-site wastewater treatment and other potential P sources within the Mattatall Lake watershed. The model predicted TP concentrations in the lake during 2016-2017 adequately, and hindcasted model simulations indicated that TP has increased by 1-2  $\mu\text{g/L}$  since 1985 (CWRS, 2017). While this increase could stimulate increased primary productivity, the bioavailability of the P entering from the watershed is not well understood. Mineral forms of P would be less bioavailable, and would be deposited within the lake sediments, while dissolved and organic

forms of P would be more directly available for biological uptake. Evidence of primary production shifts since the 1980s is needed to understand whether the increased watershed activity correlates with increased primary productivity.

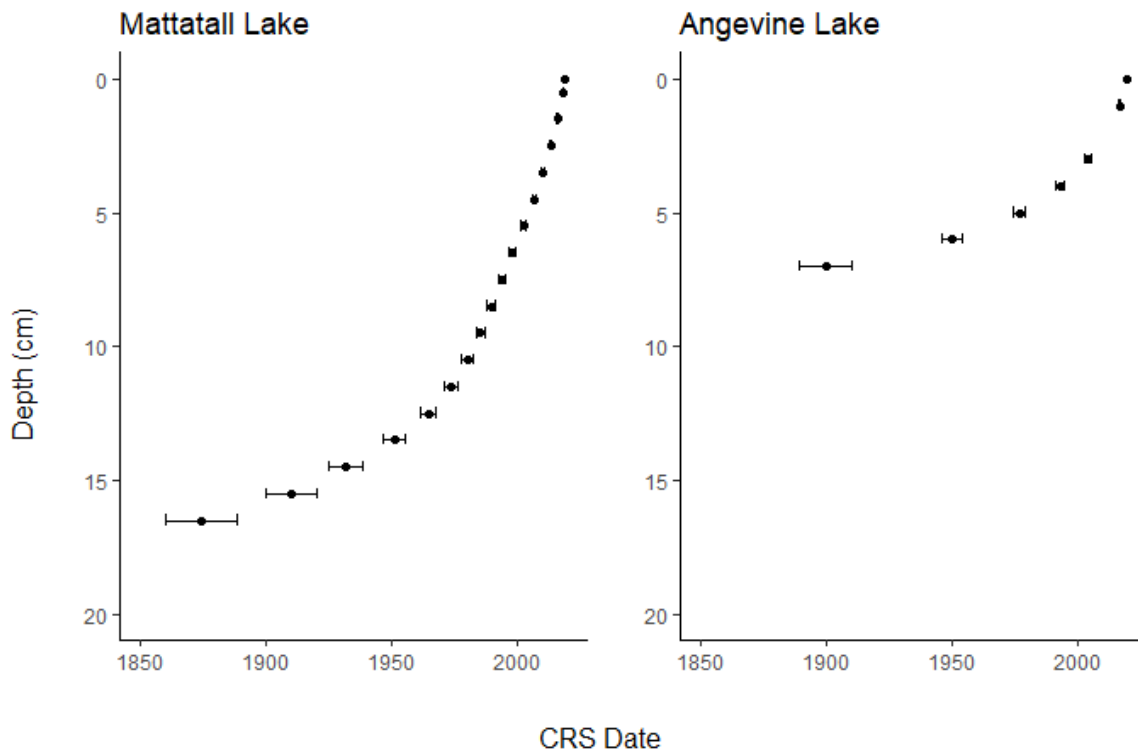
Watershed landscape changes in Mattatall Lake could have other influences on primary productivity not related to nutrient export. Reduced forest cover can generally increase the flashiness (velocity/volume) of flows moving into the lake due to increased rates of surface runoff and decreased infiltration (Thompson et al., 2009). Additionally, the residence time of water in surface and subsurface pathways in the watershed is decreased, which can also influence water chemistry. Studies have recorded water as having higher total suspended solids, TOC, P and other mineral constituents following clear cuts in watersheds (Dunnington et al., 2018; Thompson et al., 2009; Winkler et al., 2013). How these chemistry changes impact lake productivity is highly dependent on site-specific factors. In the absence of long-term water quality monitoring at Mattatall Lake, it would be speculative to ascribe any one of these potential impacts of clear cutting on water quality changes within the lake. However, it should be considered that clear cutting can lead to better HAB habitability through means beyond P export.

#### 4.4 Sediment Bulk Biogeochemistry

Analysis of the lake sediments at Mattatall and Angevine lakes included biological and geochemical proxies.

##### 4.4.1 Radiometric Dating

The radiometric dating profiles of both lakes follow an exponential decline in  $^{210}\text{Pb}$  activity. Plots of the activities of radio isotopes  $^{210}\text{Pb}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$  (bismuth) and  $^{137}\text{Cs}$  are in Appendix A. In Mattatall Lake, background levels of  $^{210}\text{Pb}$  were reached at approximately 16.5 cm, which using the CRS model, was dated at  $1874 \pm 14$  AD (Figure 4.11). In Angevine Lake, background levels of  $^{210}\text{Pb}$  were reached at approximately 7 cm, which using the CRS model, was dated as being  $1899 \pm 11$  AD (Figure 4.11). Angevine Lake generally has a lower sedimentation rate than Mattatall Lake.

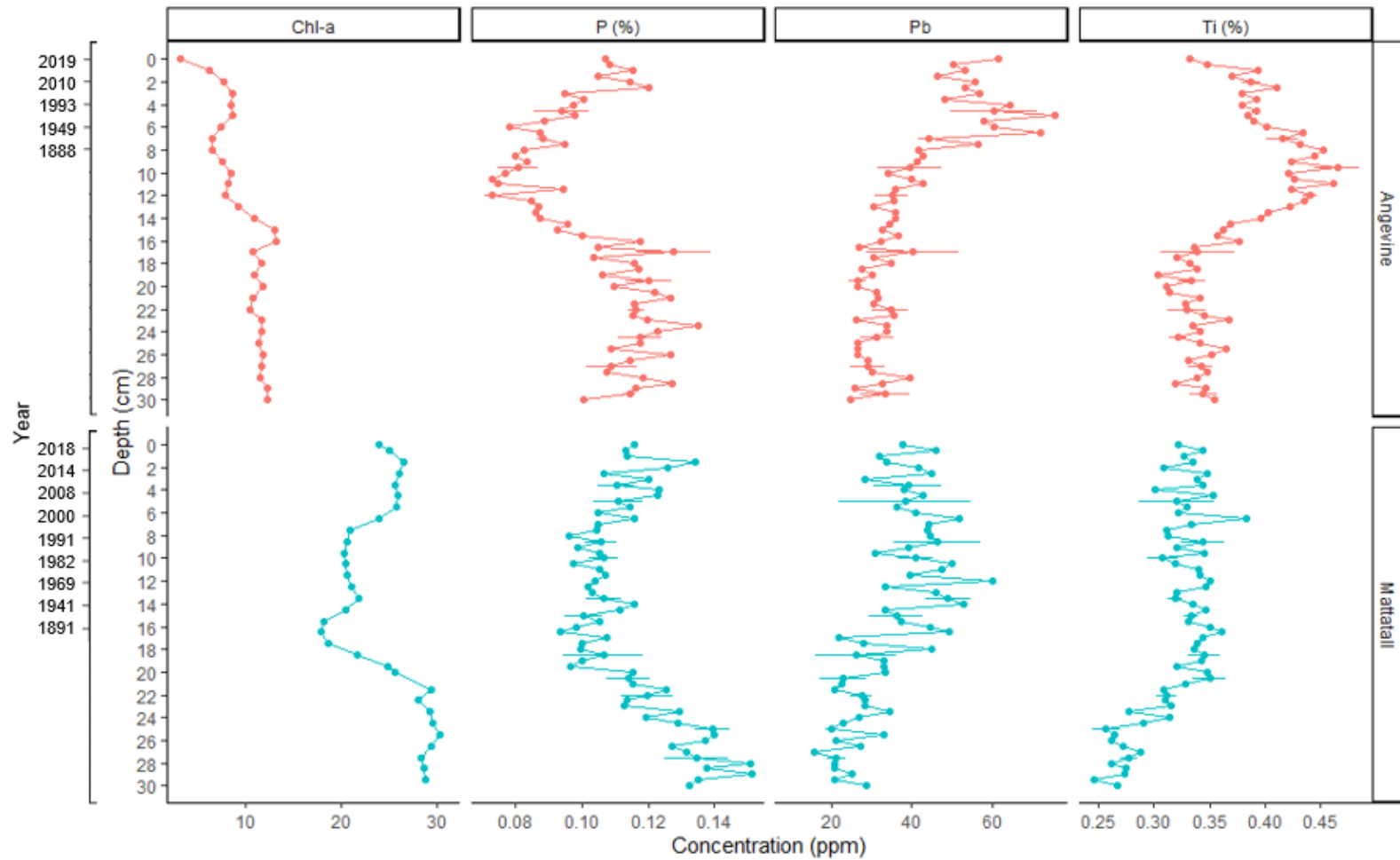


**Figure 4.11: Estimated CRS  $^{210}\text{Pb}$  date versus core depth for Mattatall and Angevine Lakes.**

#### 4.4.2 *Biogeochemistry Profiles*

The profiles of selected biogeochemical proxies for Mattatall and Angevine Lake's sediment cores are provided in Figure 4.12. Mattatall Lake's profiles are generally 'noisier' (highly variable adjacent values), which is likely a result of Mattatall Lake's higher sedimentation rate, and thus a greater sampling resolution. Mattatall Lake's high variability across samples appears to be consistent among all the elements that were graphed. Angevine Lake in contrast generally shows lower stratigraphic variability in the bulk geochemical response through time among all elements that were graphed. Consistency in values in the Angevine Lake sediment data may be attributed to slower sedimentation rate and less shoreline disturbance.

Stable Pb has been used in Nova Scotia as a tool for dating sediment cores, where across the province the peak in total Pb occurs between 1970-1980 (Dunnington, 2017). The peak in stable lead for both lake geochemical records generally agrees with dates obtained from  $^{210}\text{Pb}$ . In Mattatall Lake, the stable Pb peaked at about 10-12 cm (or 1969-1982; Figure 4.12). In Angevine Lake, the stable Pb peaked at about 4 cm (or 1993; Figure 4.12). This corroboration of the radiometric and stable Pb dating methods provides validation in the dating of these cores.



**Figure 4.12: Spectrally inferred sediment chl-a and total metals profiles for Mattatall and Angevine Lakes. Elements followed by (%) are the concentration in ppm divided by 10000.**

The Ti profile at Mattatall Lake shows low, presumably background concentrations from the base of the core until ~ 26 cm (pre-1800). An increase in Ti occurs in the early 1800s, stabilizes around 1890 to Present at a higher concentration than pre-development. The Ti profile at Angevine Lake follows a similar pattern with an increase in Ti at 15 cm (mid-1800s), and then a decrease from 2010 to Present. Titanium generally indicates a greater proportion of clastic material input from the watershed (Boyle, 2001). Titanium increases in the 1800s in both lakes, which coincides with expanding settlement and land clearing in the region. In Mattatall Lake, the increasing clastic input has persisted to top of core; this likely is associated with consistent and recurring land clearing and development in this watershed. Such activities would maintain soil mobility at the shorelines and throughout the watershed.

The stable Pb curve is not well defined in Mattatall Lake but appears to align with Ti trends. This indicates that Pb could also be supplied from the landscape as well as the atmosphere. Mineral occurrences of Pb in the Cumberland Basin region are hosted mainly in sandstone (redbed), as well as fault-related occurrences (Ryan & Boehner, 1994). Sampling in Tatamagouche, near to the study site, found measurable Pb in redbed sandstones as well as in till samples (Ryan & Boehner, 1994). Angevine Lake has a clearly defined Pb curve, which indicates that the atmospheric contribution of Pb is not being obscured by watershed processes.

The total P in Mattatall Lake is inversely related to Ti, decreasing from background levels of 13000-15000 ppm to 10000 ppm at 26-22 cm. Total P has accumulated at consistent levels from ca. 1890 to present at 10000 to 12000 ppm. This corroborates P export model evidence that external P inputs into Mattatall lake have not significantly changed despite landscape modification events in recent decades (CWRS, 2017). Phosphorus could have been diluted by the increasing influx of clastic sediment. This interpretation would suggest that the main source of P in Mattatall Lake is not clastic sediment, but rather biogenic sources such as tree leaf litter, internal cycling of P and minor additions from septic/residential activities. Total P in Angevine Lake was also inversely related to Ti. However, in Angevine Lake both P and Ti are near to pre-1800 values at the top 5 cm of the core (1993 to present), indicating that this lake could be returning to a pre-development state in terms of clastic sediment input. Landscape change in this watershed has been less intense when compared to Mattatall Lake with longer recovery periods, as evidenced by NDVI models.

Spectrally inferred sediment chl-a was relatively higher in Mattatall Lake prior to watershed development in the 1800s, chl-a concentration rapidly declined beginning at 22 cm depth (Figure 4.12). The decline occurred concurrently with decreasing P and increasing Ti. Chlorophyll-a was lowest at ca.1891 (16 cm depth) and increased steadily from that time until Present but did not reach pre-development concentrations. Angevine Lake also demonstrated higher pre-development concentrations of VRS chl-a, followed by decreasing chl-a to Present. At Angevine Lake, the chl-a does not readily appear to track with P concentrations but might correlate to increasing Ti concentrations beginning at 16 cm depth.

Overall, less chl-a is being sequestered at Present compared to pre-development concentrations for both lakes. These chl-a results are anomalous when compared to most modern lake studies where productivity has been perceived as increasing (Antoniades et al., 2011; Michelutti et al., 2005; Michelutti & Smol, 2016; Paterson et al., 2017b). Spectrally inferred sediment chl-a has been used on several lakes across Nova Scotia. Lake George in Kings County (western NS) demonstrated increasing sediment chl-a through time (Korosi et al., 2012). Primary productivity increase in Lake George was thought to be related to decreasing Ca concentrations, which in turn led to a shift in zooplankton community which decreased grazing pressure on phytoplankton (Korosi et al., 2012). Lake Trefry in southern Nova Scotia demonstrated consistently increasing chl-a concentrations since an intentional copper sulphate poisoning event in 1938 (Korosi & Smol, 2012). Nowlans Lake in southwestern Nova Scotia also demonstrated increasing chl-a relating to eutrophication from excessive P loading inferred from an adjacent mink farm (Campbell, 2021). Notably, most studies that use sediment chl-a as a proxy for productivity do so because there is concern about eutrophication. Mattatall Lake is not an exception; however, the chl-a record is unique as the inference of increasing productivity through time (eg. first observed HABs) is not clearly reflected in the sediment record.

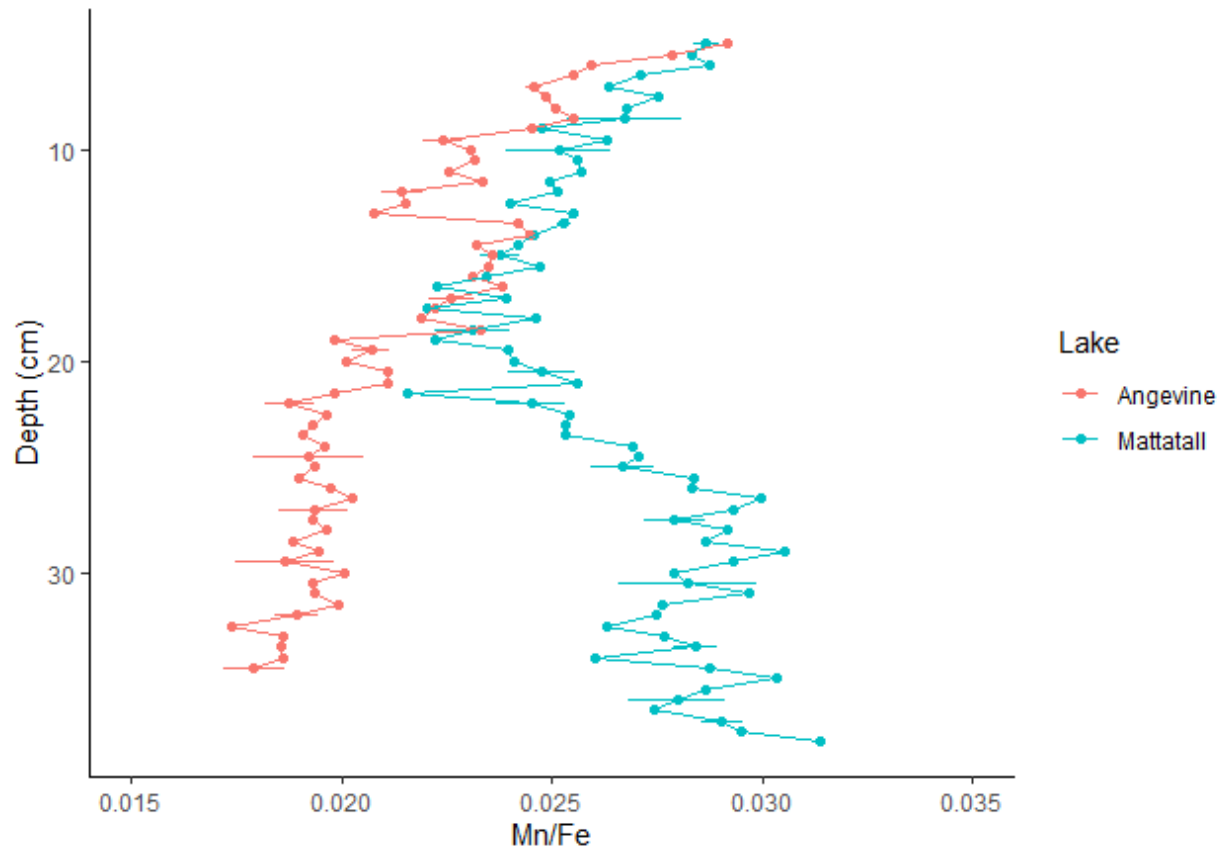
While the Mattatall Lake record is dissimilar to studies of productive meso-eutrophic lakes in Nova Scotia, the VRS chl-a pattern shares similarities with a remote, oligotrophic lake in northern Ontario. Dickson Lake also had unprecedented HABs in 2014 and 2015, and a paleolimnological study was initiated which included inferred sediment chl-a analysis (Favot et al., 2019). Like Mattatall Lake, Dickson Lake showed a decreasing chl-a trend in the late 1800s. Favot et al. (2019) attributed this to clearcutting events leading to oxygenation from enhanced

wind mixing decreasing internal loading of P and/or dilution of the chl-a signal, and not necessarily a decrease in productivity. With the increasing sedimentation rate and clastic input at Mattatall Lake (as indicated by increasing Ti and the  $^{210}\text{Pb}$  depth/time model), it is reasonable to conclude the VRS chl-a signal is likely being diluted. Where these lakes differ is that chl-a in Dickson Lake has increased over pre-development values since the ‘dilution event’ (Favot et al., 2019).

Manganese and Fe are useful geochemical tools for examining how redox conditions may have changed within the lake sediments (Mackereth & Cooper, 1966). Ratios of Mn/Fe are provided in Figure 4.13. The top 5 cm of both cores was removed from the graph because these layers are not reliable redox indicators because the accumulation of Fe and Mn in the surface sediment layers is still determined by the redox conditions at the time of sampling (Makri et al., 2021). In Mattatall Lake, the ratio of Mn/Fe is consistent until 26 cm (pre-1900), where the ratio begins to decrease in value. This change in ratio is coincident with increasing Ti. Relatively lower Mn/Fe values persist until 15 cm when the ratio steadily increases until 5 cm. The decreasing Mn/Fe at 26 cm could indicate increasingly anoxic conditions at the sediment/water interface because the Mn is being lost into solution (Davison, 1993). Decreased Mn concentrations relative to Fe could also indicate an increase in organic matter supply, which would in turn influence the redox conditions controlling Mn sequestration (Koinig et al., 2003). More information on the nature of organic matter accumulation would be needed to understand whether this is a possible mechanism at Mattatall Lake. Where this change in ratio is coincident with Ti increase, it cannot be ruled out that the shift could be related to increasing clastic material input, which would potentially obscure signals from redox shifts (Makri et al., 2021).

In Angevine Lake, Mn/Fe remain at nearly constant concentrations, suggesting both deposition and redox conditions were consistent. Mn/Fe ratios began a steady increase at about 20 cm to 5 cm, coincident with increasing Ti input. Mn/Fe does rebound to background conditions like Ti and P do. This could suggest that Angevine Lake has had increasingly oxic conditions because a greater proportion of Mn is being sequestered relative to Fe. Similar to Mattatall Lake, though, Mn/Fe ratios could be influenced by clastic material input, which would potentially obscure signals from redox shifts (Makri et al., 2021).



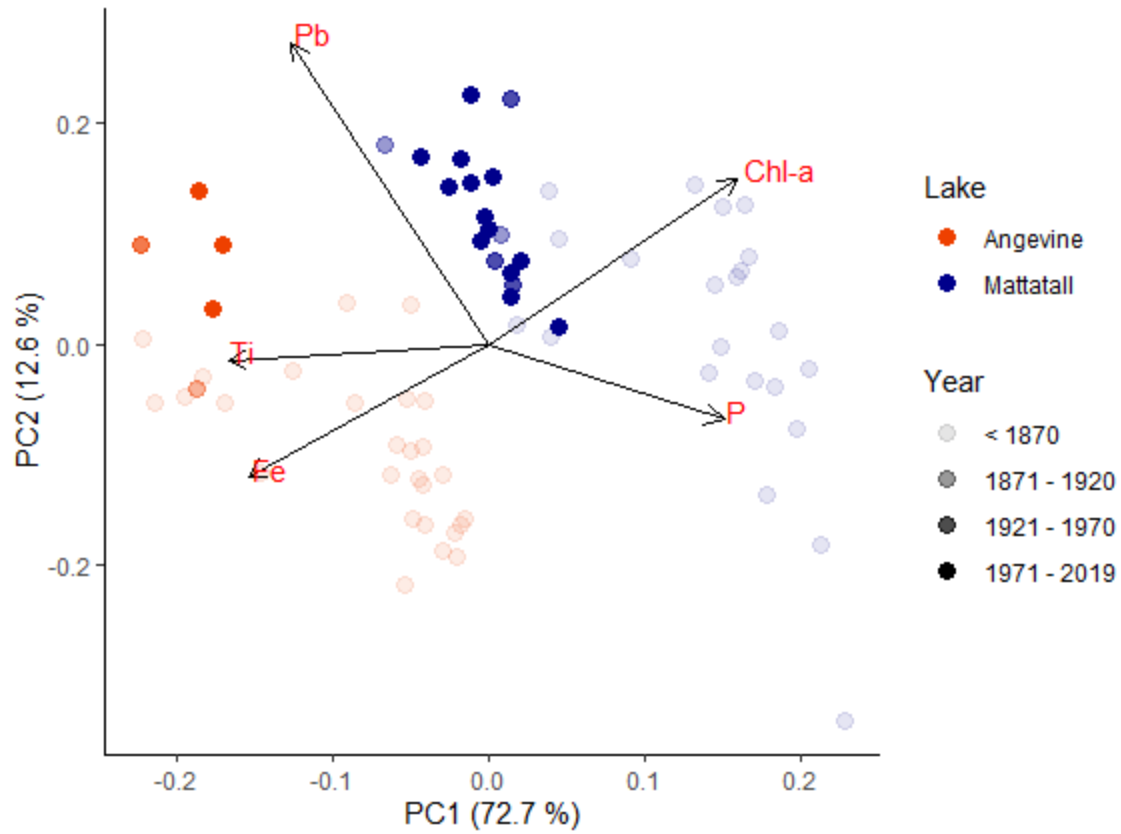


**Figure 4.13: Ratio of Mn/Fe in Mattatall and Angevine Lakes. The top 5 cm was removed to simplify interpretation.**

#### 4.4.3 *Principal Component Analysis*

A PCA was conducted to understand similarities and dissimilarities in the biogeochemistry of the Mattatall and Angevine Lake sediments across the entirety of both archives. The PCA explained 85.3 % of the variance in the dataset in the first two principal component (PC) axes. The PCA biplot (Figure 4.14) illustrates that there is a distinction between Mattatall Lake and Angevine Lake sediments along the PC1 axis, which explained 72.7 % of the variance. According to the loadings (shown as vectors on the PC plot; Figure 4.14), the PC1 axis is defined by Ti and Fe in the negative direction, and chl-a and P in the positive direction. These data demonstrated that sediments at Mattatall Lake and Angevine Lake are distinct. Although the lakes have similar watershed and water chemistry characteristics, it can be inferred that the processes influencing sediment deposition have been different. For Mattatall Lake, the sediment characteristics trend toward chl-a and P; both relate to productivity within the lake. For Angevine Lake, the sediment characteristics trend toward Ti and Fe, indicating that productivity has a less prominent role. These results suggest that Mattatall Lake has historically had higher productivity relative to Angevine Lake.

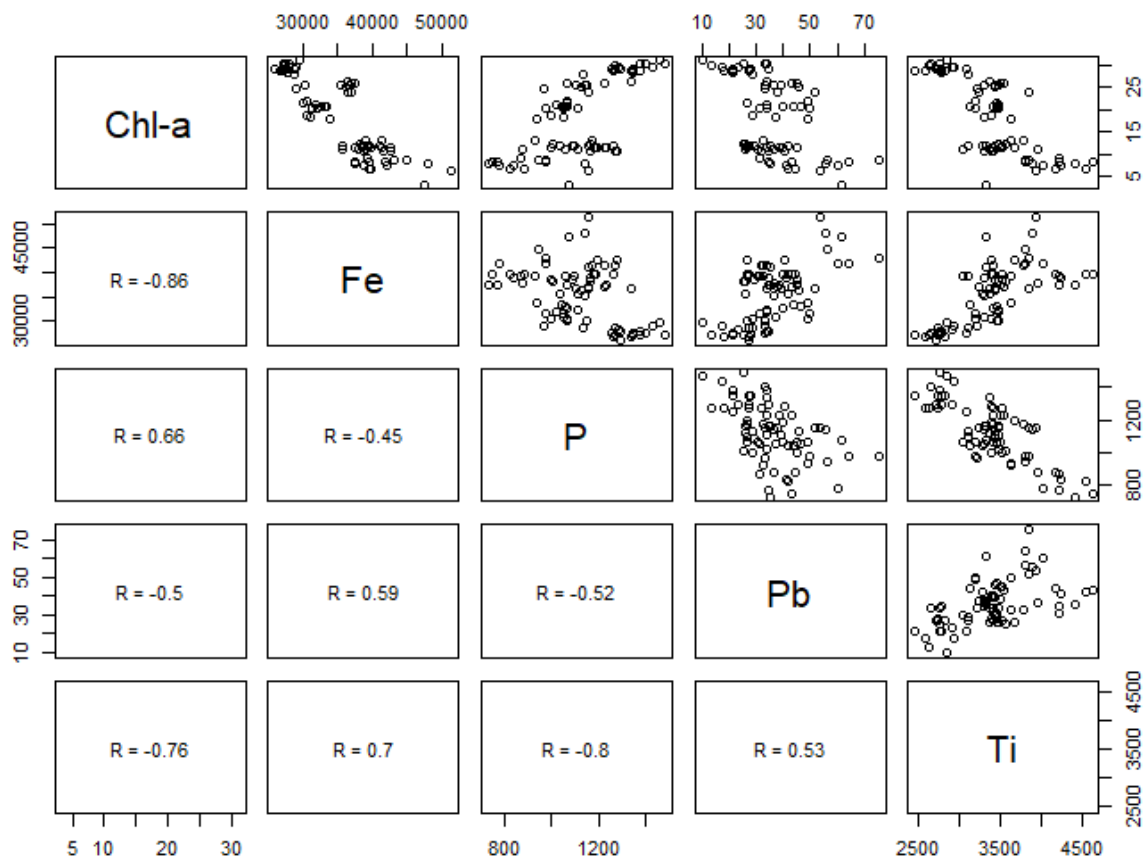
The PC2 axis explained 12.6 % of the variance, and did not further distinguish the two lakes, but rather, the timing of deposition of sediments (Figure 4.14). Modern sediments deposited from 1971-2019 cluster in the positive direction toward Pb and Ti. Sediment deposited prior to 1870 cluster in the negative direction. This gradient relates to the increasing Ti and Pb deposition in both lakes in the past 50 years which is readily apparent in the geochemical profile plots (Figure 4.12).



**Figure 4.14: PCA biplot of the Mattatall and Angevine Lakes sediment proxies. 50-year intervals until pre-1870 are denoted by colour intensity.**

#### 4.4.4 General Linear Model

Given the complexity of the VRS chl-a curve for both Mattatall and Angevine Lakes, the application of a multivariate GLM was used to help explain the relationships between chl-a and the other elements. Variable-to-variable correlations for chl-a, Fe, P, Pb and Ti were first determined using pair-plots and associated R values (Figure 4.15). Where a value of  $R > 0.7$  was considered linearly correlated, it was found that chl-a was best correlated with Fe and Ti. It was also noted that Ti correlated well with Fe and P, which was accounted for in the construction of the GLM as these parameters were assumed to be collinear, and not included in the same model.



**Figure 4.15: Pair plots of the parameters of interest are shown in the top right of the plot. Corresponding R values are reported in the bottom left of the plot.**

Several model variations were tested as described in Table 4.8, beginning with M1 (**Chl-a** ~ **Fe + P + Pb + Ti**). This model included collinear pairs and did not pass any assumptions tests. The next step was to then eliminate collinear variables, which led to M2 (**Chl-a** ~ **Fe + P +**

**Pb**) and M3 (**Chl-a** ~ **Pb** + **Ti**). M2 did not pass assumptions testing, while M3 did pass the test for linearity. To check whether the model M3 could be reduced further, a backward stepwise regression was applied. This yielded the final univariate model M4 (**Chl-a** ~ **Ti**). M4 had a p-value of < 0.05, indicating that the model was significant, and adjusted-R<sup>2</sup> of 0.533 (Table 4.8). AIC was used to compare the efficiency of the different model options. The lowest AIC is typically the best model, which maximizes accuracy and minimizes complexity. M4 had the second largest AIC since it possessed lower accuracy, but it did pass the most assumption tests which led to its selection as the best model.

The model M4 was checked against the assumptions of independence, linearity, homoscedasticity, and normality. The statistical tests applied to the model and their corresponding results/interpretation are presented in Table 4.9. Each test was considered as passing if the p-value was > 0.05. The Durbin-Watson test of independence failed. This was expected given that these data were derived from the same cores/samples of sediment. The Ramsey's RESET test for linearity and Breusch-Pagan test for homoscedasticity passed, meaning that the data contains linear relationships and variance is equal across the dataset. The Shapiro-Wilks test for normality failed, but this has been attributed to the skewed nature of the data.

M4 demonstrated that chl-a was significantly predicted and correlated negatively with Ti, as indicated by the model formula (coefficient error and significance are summarized in Table 4.10):

$$\mathbf{Chl-a = - 2.80(Ti) + 25.5}$$

This confirms the observed relationship in the profile data that as Ti increases, chl-a decreases (Figure 4.12). While this information was apparent in the pair plots (Figure 4.15), the GLM exercise aided in ruling out other variables, or combinations of variables, as being potential controls on chl-a accumulation in the sediment cores. While Fe and P did correlate with chl-a in the pair plots, they did not pass the assumption tests when put in a GLM that did not include Ti. It can be surmised that Ti, and therefore clastic deposition, has a major influence on the relative accumulation of chl-a and other elements in both Mattatall and Angevine Lakes.

**Table 4.8: GLM model variations and tests**

Name	Model	Independence Durbin-Watson	Linearity RESET	Homoscedasticity Breusch-Pagan	Normality Shapiro-Wilks	AIC	p-value	Adjusted-R2
M1	`Chl-a` ~ Fe + P + Pb + Ti	5.98E-08	5.19E-05	0.04709	0.0061	-210.1	2.20E-16	0.8
M2	`Chl-a` ~ Fe + P + Pb	1.87E-08	3.16E-05	0.02257	0.0002726	-209.24	2.20E-16	0.7951
M3	`Chl-a` ~ Pb + Ti	9.81E-13	0.5552	0.02262	0.004501	-148.98	3.52E-13	0.5366
M4	`Chl-a` ~ Ti	4.29E-10	0.6437	0.747	6.79E-04	-149.36	6.50E-14	0.533

**Table 4.9: Assumption test results and interpretations for the M4 model.**

Assumption	Test	Test result	Accept H0	Interpretation
Independence	Durbin-Watson	P = 4.29E-10	Reject	True autocorrelation is greater than 0
Linearity	Ramsey's RESET	0.6437	Accept	Variables are linearly related
Homoscedasticity	Breusch-Pagan	0.747	Accept	Variance is equal
Normality	Shapiro-Wilks	6.79E-04	Reject	Data is not normal

**Table 4.10: Summary of variable coefficients, error and significance for model M4.**

Coefficient	Estimate	Std. Error	p-value
Intercept	25.4981	2.4577	5.19E-16
Ti	-2.7981	0.3027	6.50E-14

#### 4.5 Synopsis of Results and Discussion

How these results relate and respond to each of the original research objectives outlined in the Introduction will be discussed in the following section. The outcomes of the research objectives will be used to answer the research question that guided this thesis; *Can factors contributing to HABs in Mattatall Lake be identified using an integration of environmental change study techniques?*

##### **Objective 1: Compare the contemporary water quality and the history/extent of landscape disturbance at Mattatall and Angevine Lakes.**

Contemporary water quality monitoring found that Mattatall Lake and Angevine Lake were comparable water bodies. They were both oligo-mesotrophic, neutral pH, soft watered, clear to slightly coloured, and low N. Where these lakes differ is that Mattatall Lake had slightly higher TP and chl-a concentrations. Notably, TP and chl-a were never high enough at any sampling event to classify Mattatall Lake as eutrophic, Mattatall Lake has been firmly oligo-mesotrophic for the duration of this study. Slightly higher productivity relative to Angevine Lake is not necessarily a recent development and is likely in the range of natural variation for Mattatall Lake. The PCA of sedimentary pigments and elemental data demonstrated that Mattatall Lake, for the entirety of the sediment record, is more defined by those same productivity parameters (P and chl-a) relative to Angevine Lake. This corroborates the reasoning that slightly higher productivity is not a new phenomenon, but rather a consistent state for this lake.

Landscape imagery indicated that land uses in both watersheds were similar, and therefore facilitated the assumption that regional (climate and atmospheric contaminant transport) and proximal land use stressors were similar for both lakes. Landsat images dating back to 1985 showed that land uses in the watersheds have been similar historically as well. However, NDVI analysis indicated that Mattatall Lake has historically experienced more landscape change- mainly in the form of forest removal. This is corroborated by elemental analysis where the clastic input indicator Ti increased in concentration beginning in the 1800s and has not decreased to pre-development levels. In contrast, Angevine Lake showed an increase in Ti in the 1800s, but Ti inputs decreased to predevelopment levels ca. 1993 to present. General linear modelling statistically defined Ti as an important control on the relative accumulation of chl-a and other elements for both watersheds.

The landscape change history and increased accumulation of clastic material in Mattatall Lake is typical in NS lakes (Dunnington et al., 2018; Ginn et al., 2015; Tymstra et al., 2013). It was expected that P and chl-a would increase and track with increased clastic sediment input, as has been found in similar HAB studies (Korosi et al., 2012; Korosi & Smol, 2012; Campbell, 2021). However, the elemental P and chl-a are confounding with the Ti and landscape change analysis because of their inverse relationship with Ti. The decreasing P at the same time as clastic input increasing could be explained by dilution. Indeed, the P loading model conducted in 2017 (CWRS, 2017) suggested that landscape change in combination with the soils/bedrock/forest type of Mattatall Lake was not enough to drastically increase nutrient input into the lake. Linking these two pieces of evidence, it is surmised that the watershed is not a significant source of P for Mattatall Lake and P is not being loaded along with clastic deposition. Angevine Lake shows signs of similar processes given that the P accumulation was also inversely related to Ti input.

**Research Objective 2: Explore the role of climate in regulating lake characteristics from a regional perspective.**

Long term climate records have evidenced that average annual, summer, fall and winter daily minimum temperatures have increased significantly in the past 145 years in Nova Scotia. This study did not quantify how these climate parameters might have altered lake processes in Mattatall and Angevine Lakes. Literature reviewed for this thesis suggested that it is possible that a 1 °C increase in air temperature could increase average annual surface water temperatures as well as the timing and thermal inertia of summer stratification (Butcher et al., 2015; Filazzola et al., 2020; Šporka et al., 2006). The evidence in the literature is quite compelling, but more research would need to be done in Nova Scotia to determine whether this physical impact of climate change is influencing local water bodies.

Ratios of Fe/Mn in Mattatall and Angevine Lake were evaluated as a proxy for the prevalence of hypolimnetic anoxia. Anoxia in the profundal zone of lake can potentially track with climate change impacts because it is related to lake stratification (Adrian et al., 2009). Ratios had an apparent shift in value coincident with Ti increases. In Mattatall Lake, it appeared to trend toward more anoxic conditions, with a rebound toward pre-development ratios at present. Angevine Lake had a different response, with Mn/Fe ratios trending consistently toward



oxic conditions. Where these changes are coincident with Ti influxes, it is possible that clastic influences could be obscuring redox shift signals (Makri et al., 2021), especially in Mattatall Lake where Mn/Fe tracks inversely with Ti. In contrast, Mn/Fe in Angevine Lake sediment does not readily track with Ti (i.e. does not rebound to pre-development values at top of core like Ti), therefore it is more likely that redox conditions are being observed. However, increasing oxic conditions in Angevine Lake could be related to decreasing accumulation of organic matter associated with photosynthetic biomass because consistently decreasing sediment chl-a was also observed in this core. In summary, it is not possible to deduce from these data whether climate change is influencing redox shifts. Mattatall Lake's redox conditions are potentially obscured by clastic sediment deposition, while Angevine Lake's redox conditions may be observed, but also being influenced by productivity regime shifts in this lake.

**Research Objective 3: Elucidate which factors could have led to the HABs in Mattatall Lake using a weight of evidence approach.**

It has been established that the watershed is not likely an important source of P in Mattatall Lake. This was corroborated by the 2017 P loading model (CWRS, 2017) in combination with NDVI analysis, elemental analysis of archival sediment P and reference site comparison. Therefore, landscape change is not a significant determinant of nutrients in Mattatall Lake. However, it is important to note that watershed destabilization can make the lake more vulnerable to cyanobacteria in other ways (water temperature, flushing rate, water chemistry changes, etc; Rogora et al., 2003; Trenberth, 2011). The more important regulators of nutrients in Mattatall Lake may therefore be internal cycling of P and biogenic inputs. Water quality monitoring has helped explore this possibility further.

Internal P loading was observed in Mattatall Lake during peak summer stratification through water column profiles of TP and SRP. An important distinguishing feature between Mattatall and Angevine Lake was that Mattatall Lake had measurable internal loading of SRP while Angevine Lake did not. Soluble reactive phosphorus is readily available for uptake by biological agents. If present at high enough concentrations during turn over it can aid in the rapid proliferation of a HAB (O'Neil et al., 2012). There are important factors that regulate SRP release in a lake that pertain to both the water chemistry and sediment geochemistry. Fractionating water and sediment P, Fe and S components was beyond the scope of this study.

However, it can be concluded that conditions are such that SRP can be resuspended. It is proposed that the morphometry of Mattatall Lake is an important contributor to this mechanism. Basin 1 of Mattatall Lake is deep enough to stratify and has the slowest flushing rate. These characteristics make the basin more susceptible to hypoxic hypolimnion formation and subsequent SRP resuspension. Angevine Lake has many similar qualities to Mattatall Lake but differs with respect to morphometry. This is a likely explanation as to why Angevine Lake has not had periodic trophic state deviations despite being similar to Mattatall Lake in many other respects.

In summary, there is no singular cause of HABs in Mattatall Lake, but rather, a combination of vulnerabilities that lowered the threshold for HAB proliferation. Firstly, the lakes trophic state is in the range of oligo-mesotrophy and likely always has been. It is possible that under the right conditions the lake can support sporadic algae blooms, and that this is within the range of the lake's natural variability. Secondly, the unique morphometry of Mattatall Lake contributes to the overall lake vulnerability to HABs. Basin 1 is deep enough to stratify and deplete in oxygen, and internal P loading processes were observed during summer stratification. This is an important control on P availability in Mattatall Lake, especially considering that the watershed was not found to be a significant source of P to the lake. Superimposed on these inherent characteristics and processes governing productivity in Mattatall Lake, there are climate and anthropogenic interactions. Climate change has the potential to exacerbate conditions already existing in the lake by increasing summer stratification duration, increasing surface water temperature, and making the lake more habitable to cyanobacteria. Landscape change destabilises the hydrology of the watershed and could impact lake chemistry in other ways. This study focused on mechanisms that control P input and therefore did not assess other potential impacts of landscape change on Mattatall Lake and this could be an area of future study.

**Research Objective 4: Utilize paleoenvironmental data in combination with water quality monitoring, modelling and reference site comparison and assess the efficacy of using these tools together.**

The combination of paleoenvironmental data with other forms of environmental change study was effective in assessing HAB drivers in Mattatall Lake. Multiple lines of evidence were instrumental in constraining results interpretations. Sediment geochemical analysis was useful in

determining landscape influences on bulk elemental accumulations, but it would not have been possible to identify internal loading processes from these data alone. In contrast, sediment data provided a basis of understanding the history of productivity in Mattatall Lake, which contemporary water quality monitoring was not capable of, and modelling could not verify reliably. We assume because the algae blooms were the first to be observed that there is no precedent for this level of productivity in Mattatall Lake, but human perception is limited relative to the age of a lake.

Normalized difference vegetation index modelling was informative and allowed us to summarize and quantify decades of landscape change in both watersheds. This corroborated the sediment record and previous P loading model conducted by CWRS. The collective evidence of change and how that was reflected in the sediment record was an important factor allowing us to parse the inverse relationship of Ti and P concentrations in Mattatall Lakes sediment record. Additionally, comparison to the reference site Angevine Lake provided further reassurance that this is not necessarily abnormal for the region. Lastly, the comparison to Angevine Lake was integral to understanding the importance of morphometry. It was evident how influential this intrinsic natural feature of Mattatall Lake had been to the lake's response to regional and catchment stressors as well as regulation of nutrients.

## Chapter 5 Conclusion

This study combined paleoenvironmental data with landscape change modelling, water quality monitoring and reference site evaluation along with long-term climate records to explore how cumulative impacts on Mattatall Lake may have influenced 3 HAB events of *D. planctonicum*. The integration of environmental change study techniques was effective in identifying the following key processes that likely contributed to the bloom events:

1. Productivity shifts between oligotrophy and mesotrophy are part of the natural variation of Mattatall Lake, stemming back to the beginning of sediment record before 1900.
2. Mattatall Lake has had comparatively more watershed development since the 1980s when compared to Angevine Lake. Destabilization in the watershed has led to increased clastic sediment loading into the lake, but this is not a major source of P that could have initiated the algae blooms.
3. Mattatall Lake's unique morphometry makes the lake vulnerable to anoxic stratification and subsequent internal loading of bioavailable SRP.
4. Climate change could lead to Mattatall Lake being more habitable to cyanobacteria specifically by increasing the surface water temperature and increasing the period of anoxic stratification leading to more internal nutrient loading in the summer months.

In summary, Mattatall Lake has natural attributes that have made the lake vulnerable to HABs. These include the morphometry of the lake and its related capacity to vary in its ability support primary producers. When these vulnerabilities are superimposed by watershed destabilization and climate change, the risk of HABs occurring is amplified because the threshold for cyanobacteria habitability in Mattatall Lake is lowered. These vulnerabilities could not have been discerned by any single environmental change study method in isolation or predicted by trophic state classification. While trophic state provides an elegant classification scheme to describe and compare lakes, Mattatall Lake demonstrates that there are more complex processes that can induce unpredictable deviations from trophic class.

The combination of paleoenvironmental data, modelling, monitoring and reference site comparison was integral to this study. Moreover, the use of rapid paleolimnological techniques for the purpose of integrating with other methods demonstrated the utility of bulk biogeochemical proxy analysis, even in the absence of traditional biological proxies.

Interpretation of bulk biogeochemical data alone is limited and should be done carefully to avoid making erroneous assumptions. However, when other reliable methods of understanding environmental change are used alongside the proxy data, the collective evidence synergized well and constrained interpretation. Similarly, monitoring and modelling data would not have provided as detailed and defensible information, or appropriately accounted for the natural variability of Mattatall Lake, without the paleoenvironmental data to support it.

#### *5.1.1 Recommendations for Management of Mattatall Lake*

The following is a list of short-term and long-term potential management actions that could aid in future algae bloom prevention at Mattatall Lake:

- Lakes impacted by internal loading of P can be treated with sediment capping technologies that prevent P resuspension. For example, Phoslock is a lanthanum-modified bentonite clay that has been effective in decreasing the trophic status of some lakes when deposited on top of the lake sediment (Nürnberg & LaZerte, 2016). Application of such technology could be focused on Basin 1. Depending on sedimentation rates and external P input, repeated treatment may be necessary. A cost and benefit analysis would be recommended prior to applying capping materials to assess other potential site-specific risks and mitigation strategies.
- Mechanical water aeration is another common technique applied to lakes experiencing internal P loading (Gächter & Wehrli, 1998). This is not recommended for Mattatall Lake. As discussed in the literature review, water chemistry and geochemical controls can be more important than redox conditions in the resuspension of P. As such, this technology could be a waste of time and money that would be better applied to more suitable techniques.
- Acquisition and protection of land within the watershed. Protecting forested areas of the watershed can aid in preventing erosion and hydrologic instability. Angevine Lake provides a ready example of the benefit of limiting development with its stable accumulation of elements in the sediment record. Mattatall Lake in the long-term could reap these same benefits. Encouraging private landowners to maintain a riparian area on shoreline properties would have similar long-term benefits.

### 5.1.2 *Lessons for Lake Managers and Researchers*

Through the course of this study there were many lessons learned relating to the intersection of science, engineering, and management of lake resources. These lessons come from the application of the methods described herein, but also from conversations with academic scientists, engineers, private consultants, government regulators and citizen scientists.

- There is a need and desire for wider use of paleoenvironmental data outside the realm of academia. The utility and reliability of the data is a necessary component to any environmental change study, especially for those entities most often charged with the responsibility of assessing and managing freshwater resources (government, consulting, etc). Applied research partnering with agencies in non-academic sectors provides paleoenvironmental data and information where it is vitally needed, creates funding opportunities for researchers and students, and increases awareness for the utility of paleolimnological assessment.
- Paleolimnology needs to be better advocated as widely applicable and defensible suite of methods and theory with standard procedures that can be repeated by novice practitioners. The discipline is niche and the need for paleoenvironmental data is outpacing the training and retention of practicing paleolimnologists. The writing and exporting of some methodologies along with even the most conservative data interpretations could be a great supplement to the toolkit of science and engineering practitioners across many sectors. This thesis demonstrated the utility of paleolimnology in combination with other tools and it is proposed that they could make an excellent standard component of lacustrine environmental assessments.
- Conversely, those involved in applied science, governing bodies and consulting agencies that make decisions on freshwater systems should seek to incorporate paleoenvironmental data. These data strengthen environmental change studies and provide an evidence-based precedent for natural variability in lacustrine systems that cannot be achieved as reliably by other methods.
- A weakness of this thesis was a lack of communication with local community, who would likely benefit from this knowledge and recommendations. Moreover, local and traditional knowledge holders can provide valuable insights and suggestions that can be imperative to the interpretation of data and resolve knowledge gaps.

### 5.1.3 *Future Research*

There were several knowledge gaps encountered through the course of this study that could be resolved by the following recommended research:

- The specific water and sediment chemistry controls of P resuspension in Mattatall Lake would be useful to investigate. This research would assist in determining whether aeration could be a useful tool in the future for Mattatall Lake should HAB events occur more consistently.
- Impacts of climate on ice coverage in Nova Scotia. This study demonstrated that averaged air temperatures have increased in Nova Scotia in the past hundred years. How this has impacted lakes from a regional perspective is unknown. Long term records of ice coverage are scarce; therefore, it is recommended that a modelling approach be employed. Winter average air temperatures can be used to model ice coverage on lakes and could be calibrated against existing records.
- Impacts of climate on anoxic stratification in Nova Scotia. Similar to the previous recommendation, stratification regimes through time are unknown in Nova Scotia. Modelling of stratification duration using climate records could be interpreted alongside top/bottom analysis of paleolimnological anoxia proxies on a subset of lakes such as invertebrates (Kurek et al., 2012) and Mn/Fe (Boyle, 2001).
- This study focused mainly on abiotic factors and conditions that could influence lake productivity. Another important factor to consider in future studies is the interactions of the biological community and how this can shift to increase HAB habitability in Mattatall Lake. For instance, small mouth bass have been historically introduced via stocking in both Mattatall and Angevine Lakes. The impacts of this introduction, and its cascading impacts on the zooplankton and phytoplankton community assemblage, could be explored.

## References

- Adrian, R., O'Reilly, C. M., Zagarese, H., Baines, S. B., Hessen, D. O., Keller, W., Livingstone, D. M., Sommaruga, R., Straile, D., Donk, E. V., Weyhenmeyer, G. A., & Winder, M. (2009). Lakes as sentinels of climate change. *Limnology and Oceanography*, *54*(6part2), 2283–2297. [https://doi.org/10.4319/lo.2009.54.6\\_part\\_2.2283](https://doi.org/10.4319/lo.2009.54.6_part_2.2283)
- Allen, M. R., Dube, O. P., Solecki, W., Aragón-Durand, F., Cramer, W., Humphreys, S., ... & Zickfeld, K. (2018). Framing and Context in Global Warming of 1.5 C: An IPCC Special Report on the impacts of global warming of 1.5 C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty. *Sustainable Development, and Efforts to Eradicate Poverty*. (Eds V Masson-Delmotte, P Zhai, HO Pörtner, D Roberts, J Skea, PR Shukla, A Pirani, W Moufouma-Okia, C Péan, R Pidcock, S Connors, JBR Matthews, Y Chen, X Zhou, MI Gomis, E Lonnoy, T Maycock, M Tignor, T Waterfield) pp, 41-91.
- Anderson, L. E., Krkošek, W. H., Stoddart, A. K., Trueman, B. F., & Gagnon, G. A. (2017). Lake Recovery Through Reduced Sulfate Deposition: A New Paradigm for Drinking Water Treatment. *Environmental Science & Technology*, *51*(3), 1414–1422. <https://doi.org/10.1021/acs.est.6b04889>
- Antoniades, D., Michelutti, N., Quinlan, R., Blais, J. M., Bonilla, S., Douglas, M. S. V., Pienitz, R., Smol, J. P., & Vincent, W. F. (2011). Cultural eutrophication, anoxia, and ecosystem recovery in Meretta Lake, High Arctic Canada. *Limnology and Oceanography*, *56*(2), 639–650. <https://doi.org/10.4319/lo.2011.56.2.0639>
- Appleby PG (2001) Chronostratigraphic techniques in recent sediments. In: Last WM, Smol JP (eds) Tracking environmental change using lake sediments, basin analysis, coring, and chronological techniques, vol 1. Springer, Dordrecht, pp 171–203
- Aráoz, R., Molgó, J., & Tandeau de Marsac, N. (2010). Neurotoxic cyanobacterial toxins. *Toxicon*, *56*(5), 813–828. <https://doi.org/10.1016/j.toxicon.2009.07.036>
- Arhonditsis, G. B., Brett, M. T., DeGasperi, C. L., & Schindler, D. E. (2004). Effects of climatic variability on the thermal properties of Lake Washington. *Limnology and Oceanography*, *49*(1), 256–270. <https://doi.org/10.4319/lo.2004.49.1.0256>
- Battarbee, R. W., Thrush, B. A., Clymo, R. S., Le Cren, E. D., Goldsmith, P., Mellanby, K., Bradshaw, A. D., Chester, P. F., Howells, G. D., Kerr, A., Beament, J. W. L., Bradshaw, A. D., Chester, P. F., Holdgate, M. W., Sugden, T. M., & Thrush, B. A. (1984). Diatom analysis and the acidification of lakes. *Philosophical Transactions of the Royal Society of London. B, Biological Sciences*, *305*(1124), 451–477. <https://doi.org/10.1098/rstb.1984.0070>



- Bennion, H., Hilton, J., Hughes, M., Clark, J., Hornby, D., Fozzard, I., Phillips, G., & Reynolds, C. (2005). The use of a GIS-based inventory to provide a national assessment of standing waters at risk from eutrophication in Great Britain. *Science of The Total Environment*, 344(1), 259–273. <https://doi.org/10.1016/j.scitotenv.2005.02.016>
- Binford, M. W., Deevey, E. S., & Crisman, T. L. (1983). Paleolimnology: An Historical Perspective on Lacustrine Ecosystems. *Annual Review of Ecology and Systematics*, 14, 255–286.
- Boyle, J. F. (2001). Inorganic Geochemical Methods in Palaeolimnology. In W. M. Last & J. P. Smol (Eds.), *Tracking Environmental Change Using Lake Sediments: Physical and Geochemical Methods* (pp. 83–141). Springer Netherlands. [https://doi.org/10.1007/0-306-47670-3\\_5](https://doi.org/10.1007/0-306-47670-3_5)
- Brezonik, P. L., Bouchard, R. W., Finlay, J. C., Griffin, C. G., Olmanson, L. G., Anderson, J. P., Arnold, W. A., & Hozalski, R. (2019). Color, chlorophyll a, and suspended solids effects on Secchi depth in lakes: Implications for trophic state assessment. *Ecological Applications*, 29(3), e01871. <https://doi.org/10.1002/eap.1871>
- Brylinsky, M. (2004). *User's manual for prediction of phosphorus concentration in Nova Scotia lakes: A tool for decision making* (Version 1.0). The Nova Scotia Water Quality Objectives and Model Development Steering Committee.
- Bunting, L., Leavitt, P. R., Gibson, C. E., McGee, E. J., & Hall, V. A. (2007). Degradation of water quality in Lough Neagh, Northern Ireland, by diffuse nitrogen flux from a phosphorus-rich catchment. *Limnology and Oceanography*, 52(1), 354–369. <https://doi.org/10.4319/lo.2007.52.1.0354>
- Butcher, J. B., Nover, D., Johnson, T. E., & Clark, C. M. (2015). Sensitivity of lake thermal and mixing dynamics to climate change. *Climatic Change*, 129(1), 295–305. <https://doi.org/10.1007/s10584-015-1326-1>
- Campbell, J.M. (2021). *Assessing the effects of eutrophication on lakes in southwestern Nova Scotia using subfossil remains of Chironomidae and Chaoboridae*. [Master's thesis, Mount Allison University]. Novanet.
- Canadian Council of Ministers for the Environment (CCME). (2004). *Phosphorus: Canadian guidance framework for the management of freshwater systems*. Environment Canada.
- Cantonati, M., & Lowe, R. L. (2014). Lake benthic algae: Toward an understanding of their ecology. *Freshwater Science*, 33(2), 475–486. <https://doi.org/10.1086/676140>
- Carpenter, S. R., Elser, M. M., & Elser, J. J. (1986a). Chlorophyll production, degradation, and sedimentation: Implications for paleolimnology1. *Limnology and Oceanography*, 31(1), 112–124. <https://doi.org/10.4319/lo.1986.31.1.0112>

- Carpenter, S. R., Elser, M. M., & Elser, J. J. (1986b). Chlorophyll production, degradation, and sedimentation: Implications for paleolimnology. *Limnology and Oceanography*, 31(1), 112–124. <https://doi.org/10.4319/lo.1986.31.1.0112>
- Centre for Water Resources Studies (CWRS). (2017). *Characterization of Phosphorus Sources in the Mattatall Lake Watershed*. <https://lakemattatall.ca/wp-content/uploads/2018/06/CWRS-Lake-Mattatall-Report-Executive-Summary-25-01-2018.pdf>
- Charles, D. F., Binford, M. W., Furlong, E. T., Hites, R. A., Mitchell, M. J., Norton, S. A., ..., & Wise, R. J. (1990). Paleoecological investigation of recent lake acidification in the Adirondack Mountains, N.Y. *Journal of Paleolimnology*, 3(3), 195–241.
- Chernova, E., Sidelev, S., Russkikh, I., Voyakina, E., & Zhakovskaya, Z. (2019). First observation of microcystin- and anatoxin-a-producing cyanobacteria in the easternmost part of the Gulf of Finland (the Baltic Sea). *Toxicon*, 157, 18–24. <https://doi.org/10.1016/j.toxicon.2018.11.005>
- Cohen, A. S. (2003). *Paleolimnology: The history and evolution of lake systems*. Oxford University Press.
- Das, B., Vinebrooke, R. D., Sanchez-Azofeifa, A., Rivard, B., & Wolfe, A. P. (2005). Inferring sedimentary chlorophyll concentrations with reflectance spectroscopy: A novel approach to reconstructing historical changes in the trophic status of mountain lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 62(5), 1067–1078. <https://doi.org/10.1139/f05-016>
- Davidson, K. B., Holmes, B. E. J., Spooner, I. S., Dunnington, D. W., Walker, T. R., Lake, C. B., & Su, C.-C. (2021). Application of the paleolimnological method to assess metal contaminant distribution (As, Cu, Pb, Zn) in pulp mill stabilization basin sediments, Nova Scotia, Canada. *Environmental Science and Pollution Research*. <https://doi.org/10.1007/s11356-021-14212-x>
- Davison, W. (1993). Iron and manganese in lakes. *Earth-Science Reviews*, 34(2), 119–163. [https://doi.org/10.1016/0012-8252\(93\)90029-7](https://doi.org/10.1016/0012-8252(93)90029-7)
- Deevey, E. S. (1955). The obliteration of the hypolimnion. *Mem. Ist. Ital. Idriobiol.*, 8, 6–38.
- Dodds, W. K., Jones, J. R., & Welch, E. B. (1998). Suggested classification of stream trophic state: Distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus. *Water Research*, 32(5), 1455–1462. [https://doi.org/10.1016/S0043-1354\(97\)00370-9](https://doi.org/10.1016/S0043-1354(97)00370-9)
- Dunnington, D. (2017, May 1). *A unified stable Pb sediment chronology for Halifax, Nova Scotia, Canada*. Fish & Whistle. [https://fishandwhistle.net/publication/conf\\_dunnington\\_etal17a/](https://fishandwhistle.net/publication/conf_dunnington_etal17a/)

- Dunnington, D. W. (2015). *A 500-year applied paleolimnological assessment of environmental change at Alta Lake, Whistler, British Columbia, Canada* [Acadia University]. <https://scholar.acadiau.ca/islandora/object/theses%3A411/>
- Dunnington, D. W., Spooner, I. S., Krkošek, W. H., Gagnon, G. A., Cornett, R. J., Kurek, J., White, C. E., Misiuk, B., & Tymstra, D. (2018). Anthropogenic activity in the Halifax region, Nova Scotia, Canada, as recorded by bulk geochemistry of lake sediments. *Lake and Reservoir Management*, *34*(4), 334–348. <https://doi.org/10.1080/10402381.2018.1461715>
- Dunnington, D. W., Spooner, I. S., Mallory, M. L., White, C. E., & Gagnon, G. A. (2019). Evaluating the utility of elemental measurements obtained from factory-calibrated field-portable X-Ray fluorescence units for aquatic sediments. *Environmental Pollution*, *249*, 45–53. <https://doi.org/10.1016/j.envpol.2019.03.001>
- Durkee, J., Frye, J., Fuhrmann, C., Lacke, M., Jeong, H., & Mote, T. (2008). Effects of the North Atlantic Oscillation on precipitation-type frequency and distribution in the eastern United States. *Theoretical and Applied Climatology*, *94*, 51–65. <https://doi.org/10.1007/s00704-007-0345-x>
- Enache, M. D., Paterson, A. M., & Cumming, B. F. (2011). Changes in diatom assemblages since pre-industrial times in 40 reference lakes from the Experimental Lakes Area (northwestern Ontario, Canada). *Journal of Paleolimnology*, *46*(1), 1–15. <https://doi.org/10.1007/s10933-011-9504-2>
- Engstrom, D. R., & Wright, H. E. (1984). Chemical stratigraphy of lake sediments as a record of environmental change. In E. Y. Haworth & J. W. G. Lund (Eds.), *Lake Sediments and Environmental History* (pp. 11–67). Leicester University Press.
- ESRI Inc. (2018). *ArcGIS Pro* (Version 2.3). Esri Inc. <https://www.esri.com/en-us/arcgis/products/arcgis-pro/overview>.
- ESRI Inc. (n.d.). NDVI function. Retrieved from: <https://pro.arcgis.com/en/pro-app/help/data/imagery/ndvi-function.htm>
- Favot, E. J., Rühland, K. M., DeSellas, A. M., Ingram, R., Paterson, A. M., & Smol, J. P. (2019). Climate variability promotes unprecedented cyanobacterial blooms in a remote, oligotrophic Ontario lake: Evidence from paleolimnology. *Journal of Paleolimnology*, *62*(1), 31–52. <https://doi.org/10.1007/s10933-019-00074-4>
- Field, A., Miles, J., & Field, Z. (2012). *Discovering Statistics Using R*. SAGE Publications Ltd.
- Filazzola, A., Blagrove, K., Imrit, M. A., & Sharma, S. (2020). Climate Change Drives Increases in Extreme Events for Lake Ice in the Northern Hemisphere. *Geophysical Research Letters*, *47*(18), e2020GL089608. <https://doi.org/10.1029/2020GL089608>
- Freedman, B. (2010). Chapter 20: Additional Problems of Surface Waters. In *Environmental Science: A Canadian Perspective* (5th ed., pp. 323–342). Pearson Canada Inc.

- Gächter, R., & Müller, B. (2003). Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface. *Limnology and Oceanography*, 48(2), 929–933. <https://doi.org/10.4319/lo.2003.48.2.0929>
- Gächter, R., & Wehrli, B. (1998). Ten Years of Artificial Mixing and Oxygenation: No Effect on the Internal Phosphorus Loading of Two Eutrophic Lakes. *Environmental Science & Technology*, 32(23), 3659–3665. <https://doi.org/10.1021/es980418l>
- Gallagher, L., Macdonald, R. W., & Paton, D. W. (2004). The Historical Record of Metals in Sediments from Six Lakes in the Fraser River Basin, British Columbia. *Water, Air, and Soil Pollution*, 152(1), 257–278. <https://doi.org/10.1023/B:WATE.0000015349.25371.af>
- Ginn, B. K., Rajaratnam, T., Cumming, B. F., & Smol, J. P. (2015). Establishing realistic management objectives for urban lakes using paleolimnological techniques: An example from Halifax Region (Nova Scotia, Canada). *Lake and Reservoir Management*, 31(2), 92–108. <https://doi.org/10.1080/10402381.2015.1013648>
- Glew, J. R. (1989). A new trigger mechanism for sediment samplers. *Journal of Paleolimnology*, 2(4), 241–243. <https://doi.org/10.1007/BF00195474>
- Government of Nova Scotia. (2021). *Nova Scotia Topographic DataBase—Water Features (Line Layer)* [Government]. Nova Scotia. <https://data.novascotia.ca/Lands-Forests-and-Wildlife/Nova-Scotia-Topographic-DataBase-Water-Features-Li/fpca-jrmt>
- Green, W.R., Robertson, D.M. and Wilde, F.D. (2015). *Lakes and reservoirs – Guidelines for study design and sampling: U.S. Geological Survey Techniques of Water-Resources Investigations* (book 9, chap. A10). U.S. Geological Survey. <http://dx.doi.org/10.3133/tm9a10>.
- Gunnars, A., Blomqvist, S., Johansson, P., & Andersson, C. (2002). Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. *Geochimica et Cosmochimica Acta*, 66(5), 745–758. [https://doi.org/10.1016/S0016-7037\(01\)00818-3](https://doi.org/10.1016/S0016-7037(01)00818-3)
- Hanson, P. C., Carpenter, S. R., Armstrong, D. E., Stanley, E. H., & Kratz, T. K. (2006). Lake dissolved inorganic carbon and dissolved oxygen: Changing drivers from days to decades. *Ecological Monographs*, 76(3), 343–363. [https://doi.org/10.1890/0012-9615\(2006\)076\[0343:LDICAD\]2.0.CO;2](https://doi.org/10.1890/0012-9615(2006)076[0343:LDICAD]2.0.CO;2)
- Hecky, R. E., Campbell, P., & Hendzel, L. L. (1993). The stoichiometry of carbon, nitrogen, and phosphorus in particulate matter of lakes and oceans. *Limnology and Oceanography*, 38(4), 709–724. <https://doi.org/10.4319/lo.1993.38.4.0709>
- Hupfer, M., & Lewandowski, J. (2008). Oxygen Controls the Phosphorus Release from Lake Sediments – a Long-Lasting Paradigm in Limnology. *International Review of Hydrobiology*, 93(4–5), 415–432. <https://doi.org/10.1002/iroh.200711054>

- James, W. F. (2017). Internal phosphorus loading contributions from deposited and resuspended sediment to the Lake of the Woods. *Lake and Reservoir Management*, 33(4), 347–359. <https://doi.org/10.1080/10402381.2017.1312647>
- James, W. F., Sorge, P. W., & Garrison, P. J. (2015). Managing internal phosphorus loading and vertical entrainment in a weakly stratified eutrophic lake. *Lake and Reservoir Management*, 31(4), 292–305. <https://doi.org/10.1080/10402381.2015.1079755>
- Janus, L. L., & Vollenwelder, R. A. (1981). *OECD Cooperative Programme On Eutrophication*. <https://agris.fao.org/agris-search/search.do?recordID=AV20120116325>
- Jöhnk, K. D., Huisman, J., Sharples, J., Sommeijer, B., Visser, P. M., & Stroom, J. M. (2008). Summer heatwaves promote blooms of harmful cyanobacteria. *Global Change Biology*, 14(3), 495–512. <https://doi.org/10.1111/j.1365-2486.2007.01510.x>
- Johnston, L., Hiscock, A., Holmes, B., Bermarija, T., Scott, R., Sinclair, A., & Jamieson, R. (2021). Trophic triage: A tiered eutrophication vulnerability screening tool for lakes in sparsely monitored regions. *Lake and Reservoir Management*, 0(0), 1–15. <https://doi.org/10.1080/10402381.2020.1857481>
- Jones, I. D., & Elliott, J. A. (2007). Modelling the effects of changing retention time on abundance and composition of phytoplankton species in a small lake. *Freshwater Biology*. <https://agris.fao.org/agris-search/search.do?recordID=US201300774704>
- Jones, R. I., Salonen, K., & Haan, H. D. (1988). Phosphorus transformations in the epilimnion of humic lakes: Abiotic interactions between dissolved humic materials and phosphate. *Freshwater Biology*, 19(3), 357–369. <https://doi.org/10.1111/j.1365-2427.1988.tb00357.x>
- Kelly, L. T., Champeaud, M., Beuzenberg, V., Goodwin, E., Verburg, P., & Wood, S. A. (2021). Trace metal and nitrogen concentrations differentially affect bloom forming cyanobacteria of the genus *Dolichospermum*. *Aquatic Sciences*, 83(2), 34. <https://doi.org/10.1007/s00027-021-00786-8>
- Kerekes, J. (1975). Phosphorus supply in undisturbed lakes in Kejimikujik National Park, Nova Scotia (Canada). *SIL Proceedings, 1922-2010*, 19(1), 349–357. <https://doi.org/10.1080/03680770.1974.11896074>
- Kerekes, J., Freedman, B., Beauchamp, S., & Tordon, R. (1989). Physical and chemical characteristics of three acidic, oligotrophic lakes and their watersheds in Kejimikujik National Park, Nova Scotia. *Water, Air, and Soil Pollution*, 46(1), 99–117. <https://doi.org/10.1007/BF00192848>
- Kerekes, J. J., Blouin, A. C., & Beauchamp, S. T. (1990). Trophic response to phosphorus in acidic and non-acidic lakes in Nova Scotia, Canada. *Hydrobiologia*, 191(1), 105–110. <https://doi.org/10.1007/BF00026044>
- Kleinman, P. J. A., Sharpley, A. N., McDowell, R. W., Flaten, D. N., Buda, A. R., Tao, L., Bergstrom, L., & Zhu, Q. (2011). Managing agricultural phosphorus for water quality

- protection: Principles for progress. *Plant and Soil*, 349(1), 169–182.  
<https://doi.org/10.1007/s11104-011-0832-9>
- Koinig, K. A., Shotyky, W., Lotter, A. F., Ohlendorf, C., & Sturm, M. (2003). 9000 years of geochemical evolution of lithogenic major and trace elements in the sediment of an alpine lake – the role of climate, vegetation, and land-use history. *Journal of Paleolimnology*, 30(3), 307–320. <https://doi.org/10.1023/A:1026080712312>
- Korosi, J. B., Burke, S. M., Thienpont, J. R., & Smol, J. P. (2012). Anomalous rise in algal production linked to lakewater calcium decline through food web interactions. *Proceedings of the Royal Society B: Biological Sciences*, 279(1731), 1210–1217. <https://doi.org/10.1098/rspb.2011.1411>
- Korosi, J. B., & Smol, J. P. (2012). Examining the effects of climate change, acidic deposition, and copper sulphate poisoning on long-term changes in cladoceran assemblages. *Aquatic Sciences*, 74(4), 781–792. <https://doi.org/10.1007/s00027-012-0261-8>
- Kriegler, F. J., Malila, W. A., Nalepka, R. F., & Richardson, W. (1969). Preprocessing transformations and their effects on multispectral recognition. *Remote Sensing of Environment*, VI, 97.
- Kurek, J., Kirk, J. L., Muir, D. C. G., Wang, X., Evans, M. S., & Smol, J. P. (2013). Legacy of a half century of Athabasca oil sands development recorded by lake ecosystems. *Proceedings of the National Academy of Sciences*, 110(5), 1761–1766. <https://doi.org/10.1073/pnas.1217675110>
- Kurek, J., Lawlor, L., Cumming, B. F., & Smol, J. P. (2012). Long-term oxygen conditions assessed using chironomid assemblages in brook trout lakes from Nova Scotia, Canada. *Lake and Reservoir Management*, 28(3), 177–188. <https://doi.org/10.1080/07438141.2012.692462>
- Landres, P. B., Morgan, P., & Swanson, F. J. (1999). Overview of the Use of Natural Variability Concepts in Managing Ecological Systems. *Ecological Applications*, 9(4), 1179–1188. [https://doi.org/10.1890/1051-0761\(1999\)009\[1179:OOTUON\]2.0.CO;2](https://doi.org/10.1890/1051-0761(1999)009[1179:OOTUON]2.0.CO;2)
- Last, W. M. (2001). Mineralogical analysis of lake sediments. In W. M. Last & J. P. Smol (Eds.), *Tracking Environmental Change Using Lake Sediments: Physical and Geochemical Methods* (pp. 83–141). Springer Netherlands. [https://doi.org/10.1007/0-306-47670-3\\_5](https://doi.org/10.1007/0-306-47670-3_5)
- Leavitt, P. R., & Hodgson, D. A. (2001). Sedimentary Pigments. In J. P. Smol, H. J. B. Birks, W. M. Last, R. S. Bradley, & K. Alverson (Eds.), *Tracking Environmental Change Using Lake Sediments: Terrestrial, Algal, and Siliceous Indicators* (pp. 295–325). Springer Netherlands. [https://doi.org/10.1007/0-306-47668-1\\_15](https://doi.org/10.1007/0-306-47668-1_15)
- Lennox, B., Spooner, I., Jull, T., & Patterson, W. P. (2010). Post-glacial climate change and its effect on a shallow dimictic lake in Nova Scotia, Canada. *Journal of Paleolimnology*, 43(1), 15–27. <https://doi.org/10.1007/s10933-009-9310-2>

- Levine, S. N., & Schindler, D. W. (2011). Phosphorus, Nitrogen, and Carbon Dynamics of Experimental Lake 303 during Recovery from Eutrophication. *Canadian Journal of Fisheries and Aquatic Sciences*. <https://doi.org/10.1139/f89-001>
- Levine, S. N., Stainton, M. P., & Schindler, D. W. (1986). A Radiotracer Study of Phosphorus Cycling in a Eutrophic Canadian Shield Lake, Lake 227, Northwestern Ontario. *Canadian Journal of Fisheries and Aquatic Sciences*. <https://doi.org/10.1139/f86-047>
- Lorenzen CJ, Jeffrey SW (1980) Determination of chlorophyll in sea water. UNESCO Reports Technical Papers in Marine Science, vol 35.
- Lyche-Solheim, A., Feld, C. K., Birk, S., Phillips, G., Carvalho, L., Morabito, G., Mischke, U., Willby, N., Søndergaard, M., Hellsten, S., Kolada, A., Mjelde, M., Böhmer, J., Miler, O., Pusch, M. T., Argillier, C., Jeppesen, E., Lauridsen, T. L., & Poikane, S. (2013). Ecological status assessment of European lakes: A comparison of metrics for phytoplankton, macrophytes, benthic invertebrates and fish. *Hydrobiologia*, 704(1), 57–74. <https://doi.org/10.1007/s10750-012-1436-y>
- Mackereth, F. J. H., & Cooper, L. H. N. (1966). Some chemical observations on post-glacial lake sediments. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, 250(765), 165–213. <https://doi.org/10.1098/rstb.1966.0001>
- MacLeod, A., & Korycinska, A. (2019). Detailing Köppen–Geiger climate zones at sub-national to continental scale: A resource for pest risk analysis. *EPPO Bulletin*, 49(1), 73–82. <https://doi.org/10.1111/epp.12549>
- Makri, S., Wienhues, G., Bigalke, M., Gilli, A., Rey, F., Tinner, W., Vogel, H., & Grosjean, M. (2021). Variations of sedimentary Fe and Mn fractions under changing lake mixing regimes, oxygenation and land surface processes during Late-glacial and Holocene times. *Science of The Total Environment*, 755, 143418. <https://doi.org/10.1016/j.scitotenv.2020.143418>
- McHenry, L. J. (2009). Element mobility during zeolitic and argillic alteration of volcanic ash in a closed-basin lacustrine environment: Case study Olduvai Gorge, Tanzania. *Chemical Geology*, 265(3), 540–552. <https://doi.org/10.1016/j.chemgeo.2009.05.019>
- Meyers, P. A., & Teranes, J. L. (2001). Sediment organic matter. In W. M. Last & J. P. Smol (Eds.), *Tracking Environmental Change Using Lake Sediments: Physical and Geochemical Methods* (pp. 83–141). Springer Netherlands. [https://doi.org/10.1007/0-306-47670-3\\_5](https://doi.org/10.1007/0-306-47670-3_5)
- Michelutti, N., Blais, J. M., Cumming, B. F., Paterson, A. M., Rühland, K., Wolfe, A. P., & Smol, J. P. (2010). Do spectrally inferred determinations of chlorophyll a reflect trends in lake trophic status? *Journal of Paleolimnology*, 43(2), 205–217. <https://doi.org/10.1007/s10933-009-9325-8>

- Michelutti, N., Douglas, M. S. V., & Smol, J. P. (2003). Diatom response to recent climatic change in a high arctic lake (Char Lake, Cornwallis Island, Nunavut). *Global and Planetary Change*, 38(3), 257–271. [https://doi.org/10.1016/S0921-8181\(02\)00260-6](https://doi.org/10.1016/S0921-8181(02)00260-6)
- Michelutti, N., & Smol, J. P. (2016). Visible spectroscopy reliably tracks trends in paleo-production. *Journal of Paleolimnology*, 56(4), 253–265. <https://doi.org/10.1007/s10933-016-9921-3>
- Michelutti, N., Wolfe, A. P., Vinebrooke, R. D., Rivard, B., & Briner, J. P. (2005). Recent primary production increases in arctic lakes. *Geophysical Research Letters*, 32(19), Article 19. <https://doi.org/10.1029/2005GL023693>
- Milton, J. (2015, March 4). *Tatamagouche*. The Canadian Encyclopedia. <https://www.thecanadianencyclopedia.ca/en/article/tatamagouche>
- Minns, C. K., & Moore, J. E. (1992). Predicting the impact of climate change on the spatial pattern of freshwater fish yield capability in eastern Canadian lakes. *Climatic Change*, 22(4), 327–346. <https://doi.org/10.1007/BF00142432>
- Mrdjen, I. (2018). *Harmful Algal Blooms in Small Lakes: Causes, Health Risks, and Novel Exposure Prevention Strategies* [The Ohio State University]. [https://etd.ohiolink.edu/pg\\_10?0::NO:10:P10\\_ACCESSION\\_NUM:osu1531135626251706](https://etd.ohiolink.edu/pg_10?0::NO:10:P10_ACCESSION_NUM:osu1531135626251706)
- Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, 27, 31–36. [https://doi.org/10.1016/S0003-2670\(00\)88444-5](https://doi.org/10.1016/S0003-2670(00)88444-5)
- Murphy, T. P., Hall, K. J., & Yesaki, I. (1983). Coprecipitation of phosphate with calcite in a naturally eutrophic lake. *Limnology and Oceanography*, 28(1), 58–69. <https://doi.org/10.4319/lo.1983.28.1.0058>
- Naeher, S., Gilli, A., North, R. P., Hamann, Y., & Schubert, C. J. (2013). Tracing bottom water oxygenation with sedimentary Mn/Fe ratios in Lake Zurich, Switzerland. *Chemical Geology*, 352, 125–133. <https://doi.org/10.1016/j.chemgeo.2013.06.006>
- Nesse, W. D. (2012). *Introduction to mineralogy* (2nd ed.). Oxford University Press.
- Nguyen-Quang, T., Lieou, K. C., Hushchyna, K., Nguyen, T. D., Sharifi, M. N., Nadeem, M., McLellan, K., Murdymootoo, K. K., Merks, E., & Hirtle, R. (2016). The first step to sketch the spatio-temporal evolution of biochemical and physical parameters involving in the Harmful Algal Blooms (HAB) in Mattatall Lake (Nova Scotia, Canada). *Environmental Problems*, 1, Num. 1, 1–18.
- Norton, S., Fernandez, I., Amirbahman, A., Coolidge, K., & Navratil, T. (2006). Aluminum, phosphorus, and oligotrophy- assembling the pieces of the puzzle. *Internationale Vereinigung Für Theoretische Und Angewandte Limnologie: Verhandlungen*, 29(4), 1877–1886.



- Nova Scotia Department of Natural Resources (NSDNR). (2006). Bedrock geology map of the Province of Nova Scotia; Map DP ME 43, Version 2
- Nova Scotia Environment. (2017). *Protected Areas: Angevine Lake*. Province of Nova Scotia. [https://novascotia.ca/nse/protectedareas/nr\\_angevinelake.asp](https://novascotia.ca/nse/protectedareas/nr_angevinelake.asp)
- Nowland, J.L., & MacDougall, J.I. (1973). Soils of Cumberland County, Nova Scotia. Department of Agriculture. Ottawa, Ontario.
- Nriagu, J. O. (1990). The rise and fall of leaded gasoline. *Science of The Total Environment*, 92, 13–28. [https://doi.org/10.1016/0048-9697\(90\)90318-O](https://doi.org/10.1016/0048-9697(90)90318-O)
- Nürnberg, G. K. (1994). Phosphorus release from anoxic sediments: What we know and how we can deal with it. *Limnetica*, 10(1), 1–4.
- Nürnberg, G. K. (1995). Quantifying anoxia in lakes. *Limnology and Oceanography*, 40(6), 1100–1111. <https://doi.org/10.4319/lo.1995.40.6.1100>
- Nürnberg, G. K., Fischer, R., & Paterson, A. M. (2018). Reduced phosphorus retention by anoxic bottom sediments after the remediation of an industrial acidified lake area: Indications from P, Al, and Fe sediment fractions. *Science of The Total Environment*, 626, 412–422. <https://doi.org/10.1016/j.scitotenv.2018.01.103>
- Nürnberg, G. K., & LaZerte, B. D. (2016). Trophic state decrease after lanthanum-modified bentonite (Phoslock) application to a hyper-eutrophic polymictic urban lake frequented by Canada geese (*Branta canadensis*). *Lake and Reservoir Management*, 32(1), 74–88. <https://doi.org/10.1080/10402381.2015.1133739>
- Nürnberg, G. K., Tarvainen, M., Ventelä, A.-M., & Sarvala, J. (2012). Internal phosphorus load estimation during biomanipulation in a large polymictic and mesotrophic lake. *Inland Waters*, 2(3), 147–162. <https://doi.org/10.5268/IW-2.3.469>
- O’Neil, J. M., Davis, T. W., Burford, M. A., & Gobler, C. J. (2012). The rise of harmful cyanobacteria blooms: The potential roles of eutrophication and climate change. *Harmful Algae*, 14, 313–334. <https://doi.org/10.1016/j.hal.2011.10.027>
- Paerl, H. W. (2014). Mitigating harmful cyanobacterial blooms in a human- and climatically-impacted world. *Life*, 4(4), 988–1012. <https://doi.org/10.3390/life4040988>
- Paerl, H. W., & Huisman, J. (2008). Blooms like it hot. *Science*, 320(5872), 57–58. <https://doi.org/10.1126/science.1155398>
- Paerl, H. W., & Huisman, J. (2009). Climate change: A catalyst for global expansion of harmful cyanobacterial blooms. *Environmental Microbiology Reports*, 1(1), 27–37. <https://doi.org/10.1111/j.1758-2229.2008.00004.x>
- Papageorgiou, G. C. (Ed.). (2007). *Chlorophyll a fluorescence: A signature of photosynthesis* (Vol. 19). Springer Science & Business Media.

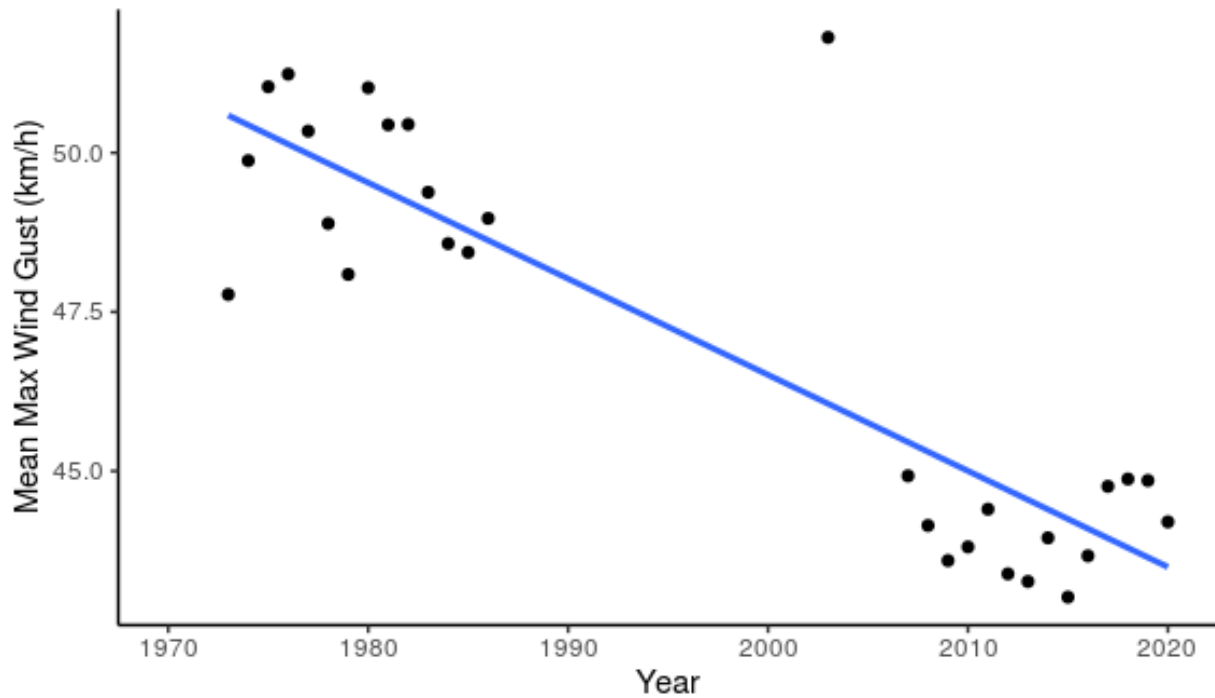
- Paterson, A. M., Rühland, K. M., Anstey, C. V., & Smol, J. P. (2017a). Climate as a driver of increasing algal production in Lake of the Woods, Ontario, Canada. *Lake and Reservoir Management*, 33(4), 403–414. <https://doi.org/10.1080/10402381.2017.1379574>
- Paterson, A. M., Rühland, K. M., Anstey, C. V., & Smol, J. P. (2017b). Climate as a driver of increasing algal production in Lake of the Woods, Ontario, Canada. *Lake and Reservoir Management*, 33(4), 403–414. <https://doi.org/10.1080/10402381.2017.1379574>
- Peck, J. (2016). *Multivariate Analysis for Community Ecologists: Step-by-Step* (2nd ed.). MJM Software.
- Pilla, R. M., Williamson, C. E., Adamovich, B. V., Adrian, R., Anneville, O., Chandra, S., Colom-Montero, W., Devlin, S. P., Dix, M. A., Dokulil, M. T., Gaiser, E. E., Girdner, S. F., Hambright, K. D., Hamilton, D. P., Havens, K., Hessen, D. O., Higgins, S. N., Huttula, T. H., Huuskonen, H., ... Zadereev, E. (2020). Deeper waters are changing less consistently than surface waters in a global analysis of 102 lakes. *Scientific Reports*, 10(1), 20514. <https://doi.org/10.1038/s41598-020-76873-x>
- R Core Team (2021). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <https://www.R-project.org/>.
- Regel, R. H., Brookes, J. D., & Ganf, G. G. (2004). Vertical migration, entrainment and photosynthesis of the freshwater dinoflagellate *Peridinium cinctum* in a shallow urban lake. *Journal of Plankton Research*, 26(2), 143–157. <https://doi.org/10.1093/plankt/fbh008>
- Rogora, M., Mosello, R., & Arisci, S. (2003). The Effect of Climate Warming on the Hydrochemistry of Alpine Lakes. *Water, Air, and Soil Pollution*, 148(1), 347–361. <https://doi.org/10.1023/A:1025489215491>
- Ryan, R. J., & Boehner, R. C. (1994). *Geology of the Cumberland Basin, Cumberland, Colchester and Pictou Counties, Nova Scotia* (Memoir 10). Nova Scotia Department of Natural Resources, Mines and Energy Branch. <https://novascotia.ca/natr/meb/pdf/memoir10.asp>
- Schaller, T., Moor, H. C., & Wehrli, B. (1997). Sedimentary profiles of Fe, Mn, V, Cr, As and Mo as indicators of benthic redox conditions in Baldeggersee. *Aquatic Sciences*, 59(4), 345–361.
- Schelske, C. L., Peplow, A., Brenner, M., & Spencer, C. N. (1994). Low-background gamma counting: Applications for <sup>210</sup>Pb dating of sediments. *Journal of Paleolimnology*, 10(2), 115–128. <https://doi.org/10.1007/BF00682508>
- Schindler, D. W. (1977). Evolution of Phosphorus Limitation in Lakes. *Science*, 195(4275), 260–262.

- Schindler, D. W. (1978). Factors regulating phytoplankton production and standing crop in the world's freshwaters. *Limnology and Oceanography*, 23(3), 478–486. <https://doi.org/10.4319/lo.1978.23.3.0478>
- Schindler, D. W. (1990). Experimental Perturbations of Whole Lakes as Tests of Hypotheses concerning Ecosystem Structure and Function. *Oikos*, 57(1), 25–41. <https://doi.org/10.2307/3565733>
- Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., Beaty, K. G., Lyng, M., & Kasian, S. E. M. (2008). Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences*, 105(32), 11254–11258. <https://doi.org/10.1073/pnas.0805108105>
- Scott, R., Goulden, T., Letman, M., Hayward, J., & Jamieson, R. (2019). Long-term evaluation of the impact of urbanization on chloride levels in lakes in a temperate region. *Journal of Environmental Management*, 244, 285–293. <https://doi.org/10.1016/j.jenvman.2019.05.029>
- Shoaf, W. T., & Lium, B. W. (1976). Improved extraction of chlorophyll a and b from algae using dimethyl sulfoxide. *Limnology and Oceanography*, 21(6), 926–928. <https://doi.org/10.4319/lo.1976.21.6.0926>
- Smol, J. P. (1992). Paleolimnology: An important tool for effective ecosystem management. *Journal of Aquatic Ecosystem Health*, 1(1), 49–58.
- Smol, J. P. (2008). *Pollution of Lakes and Rivers: A Paleoenvironmental Perspective* (2nd ed.). Blackwell Publishing.
- Šporka, F., Livingstone, D., Stuchlík, E., Turek, J., & Galas, J. (2006). Water temperatures and ice cover in lakes of the Tatra Mountains. *Biologia*, 61(18), S77–S90. <https://doi.org/10.2478/s11756-006-0121-x>
- Steffen, M. M., Belisle, B. S., Watson, S. B., Boyer, G. L., & Wilhelm, S. W. (2014). Status, causes and controls of cyanobacterial blooms in Lake Erie. *Journal of Great Lakes Research*, 40(2), 215–225. <https://doi.org/10.1016/j.jglr.2013.12.012>
- Sterling, S. M., MacLeod, S., Rotteveel, L., Hart, K., Clair, T. A., Halfyard, E. A., & O'Brien, N. L. (2020). Ionic aluminium concentrations exceed thresholds for aquatic health in Nova Scotian rivers, even during conditions of high dissolved organic carbon and low flow. *Hydrology and Earth System Sciences*, 24(10), 4763–4775. <https://doi.org/10.5194/hess-24-4763-2020>
- Tammeorg, O., Horppila, J., Tammeorg, P., Haldna, M., & Niemistö, J. (2016). Internal phosphorus loading across a cascade of three eutrophic basins: A synthesis of short- and long-term studies. *Science of The Total Environment*, 572, 943–954. <https://doi.org/10.1016/j.scitotenv.2016.07.224>

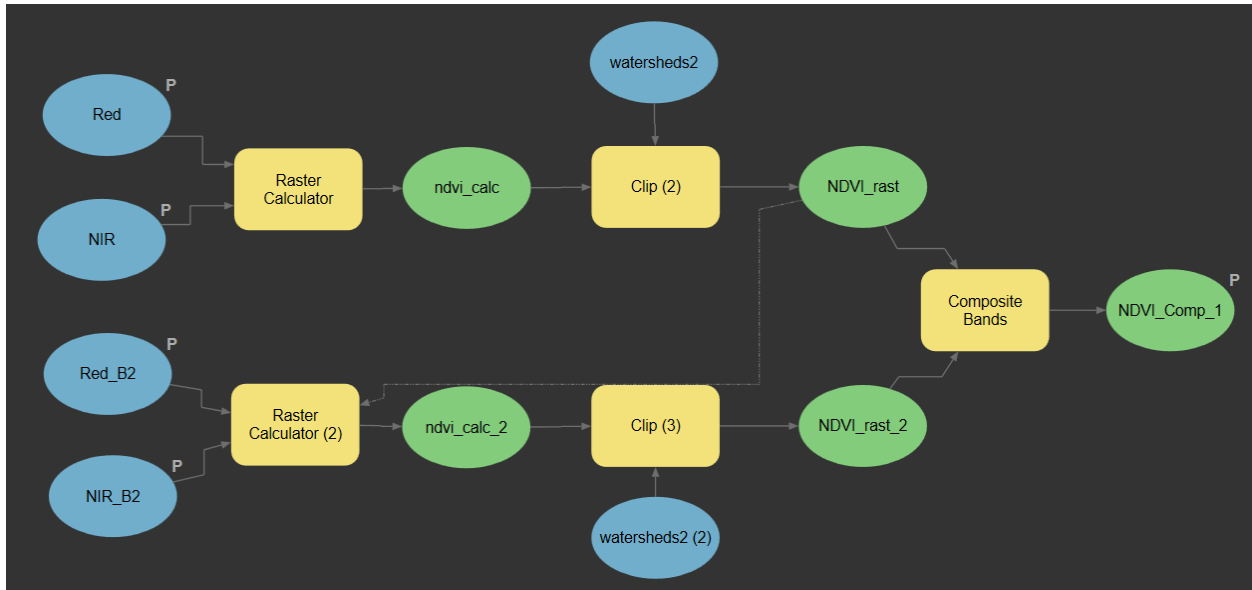
- Tammeorg, O., Möls, T., Niemistö, J., Holmroos, H., & Horppila, J. (2017). The actual role of oxygen deficit in the linkage of the water quality and benthic phosphorus release: Potential implications for lake restoration. *Science of The Total Environment*, 599–600, 732–738. <https://doi.org/10.1016/j.scitotenv.2017.04.244>
- Thompson, R. M., Phillips, N. R., & Townsend, C. R. (2009). Biological consequences of clear-cut logging around streams—Moderating effects of management. *Forest Ecology and Management*, 257(3), 931–940. <https://doi.org/10.1016/j.foreco.2008.10.025>
- Trenberth, K. E. (2011). Changes in precipitation with climate change. *Climate Research*, 47(1–2), 123–138. <https://doi.org/10.3354/cr00953>
- Tymstra, D., Spooner, I., & White, C. (2013). A paleolimnological record of anthropogenic impact on water quality in First Lake, Lower Sackville, Nova Scotia [Abstract]. *Atlantic Geology*, 49(1), 49.
- Underwood, J. K., & Schwartz, P. Y. (1990). Estimates of the numbers and areas of acidic lakes in Nova Scotia. *Proc. N.S. Inst. Sci.*, 39(1), 11-17. <https://DalSpace.library.dal.ca/handle/10222/34635>
- United States Geological Survey (USGS). (n.d.). Landsat imagery. Retrieved from: <https://earthexplorer.usgs.gov/>
- USGS. (n.d.). Landsat Missions: Landsat 5. Retrieved from: [https://www.usgs.gov/land-resources/nli/landsat/landsat-5?qt-science\\_support\\_page\\_related\\_con=0#qt-science\\_support\\_page\\_related\\_con](https://www.usgs.gov/land-resources/nli/landsat/landsat-5?qt-science_support_page_related_con=0#qt-science_support_page_related_con)
- Vahtera, E., Conley, D. J., Gustafsson, B. G., Kuosa, H., Pitkänen, H., Savchuk, O. P., Tamminen, T., Viitasalo, M., Voss, M., Wasmund, N., & Wulff, F. (2007). Internal Ecosystem Feedbacks Enhance Nitrogen-fixing Cyanobacteria Blooms and Complicate Management in the Baltic Sea. *AMBIO: A Journal of the Human Environment*, 36(2), 186–195. [https://doi.org/10.1579/0044-7447\(2007\)36\[186:IEFENC\]2.0.CO;2](https://doi.org/10.1579/0044-7447(2007)36[186:IEFENC]2.0.CO;2)
- Vincent, L. A., Wang, X. L., Milewska, E. J., Wan, H., Yang, F., & Swail, V. (2012). A second generation of homogenized Canadian monthly surface air temperature for climate trend analysis. *Journal of Geophysical Research: Atmospheres*, 117(D18). <https://doi.org/10.1029/2012JD017859>
- Vollenweider, R. A., & Kerekes, J. (1982). Eutrophication of waters. Monitoring, assessment and control. Organization for Economic Co-Operation and Development (OECD), Paris, 156.
- von Gunten, H. R., Sturm, M., & Moser, R. N. (1997). 200-Year Record of Metals in Lake Sediments and Natural Background Concentrations. *Environmental Science & Technology*, 31(8), 2193–2197. <https://doi.org/10.1021/es960616h>
- Walker, I. R. (1987). Chironomidae (Diptera) in paleoecology. *Quaternary Science Reviews*, 6(1), 29–40. [https://doi.org/10.1016/0277-3791\(87\)90014-X](https://doi.org/10.1016/0277-3791(87)90014-X)

- Warwick, W. F. (1980). Chironomidae (Diptera) responses to 2800 years of cultural influence: A paleolimnological study with special reference to sedimentation, eutrophication, and contamination processes. *The Canadian Entomologist*, *112*(11), 1193–1238. <https://doi.org/10.4039/Ent1121193-11>
- Webb, K.T., Thompson, R.L., Beke, G.J., & Nowland, J.L. (1991). Soils of Colchester County, Nova Scotia. Nova Scotia Soil Survey, Research Branch, Agriculture Canada, Report no. 19. Halifax, Nova Scotia.
- Welschmeyer N.A. (1994). Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and phaeopigments. *Limnol Oceanogr* *39*:1985-1992
- Whittington, J., Sherman, B., Green, D., & Oliver, R. L. (2000). Growth of *Ceratium hirundinella* in a subtropical Australian reservoir: The role of vertical migration. *Journal of Plankton Research*, *22*(6), 1025–1045. <https://doi.org/10.1093/plankt/22.6.1025>
- Williamson, C. E., Morris, D. P., Pace, M. L., & Olson, O. G. (1999). Dissolved organic carbon and nutrients as regulators of lake ecosystems: Resurrection of a more integrated paradigm. *Limnology and Oceanography*, *44*(3part2), 795–803. [https://doi.org/10.4319/lo.1999.44.3\\_part\\_2.0795](https://doi.org/10.4319/lo.1999.44.3_part_2.0795)
- Winkler, G., Leclerc, V., Sirois, P., Archambault, P., & Berube, P. (2013). 24- Short-term impact of forest harvesting on water quality and zooplankton communities in oligotrophic headwater lakes of the eastern Canadian Boreal Shield. *Boreal Environment Research*, *14*, 323–337.
- Yan, N. D., Keller, W., Scully, N. M., Lean, D. R. S., & Dillon, P. J. (1996). Increased UV-B penetration in a lake owing to drought-induced acidification. *Nature*, *381*(6578), 141–143. <https://doi.org/10.1038/381141a0>
- Zhang, J., Hudson, J., Neal, R., Sereda, J., Clair, T., Turner, M., Jeffries, D., Dillon, P., Molot, L., Somers, K., & Hesslein, R. (2010). Long-term patterns of dissolved organic carbon in lakes across eastern Canada: Evidence of a pronounced climate effect. *Limnology and Oceanography*, *55*(1), 30–42. <https://doi.org/10.4319/lo.2010.55.1.0030>

## APPENDIX A – SUPPLEMENTAL FIGURES



**Figure A.1: Available mean max wind gust data. The 1970-1990 cluster is from a Truro climate station, while the 2000-2020 cluster is from a Debert climate station. This figure demonstrated that wind gusts are highly influenced by the station location, and regression analysis would not reliably predict broad changes in wind speed on a climactic scale.**



**Figure A.2: Composite band model created on ArcGIS Pro (ESRI Inc., 2018) to calculate NDVI values for the Mattatall and Angevine Lake watersheds.**



**Figure A.3: Model used to subtract the NDVI raster layer values using the Greater Than Equal function on ArcGIS Pro (ESRI Inc., 2018).**

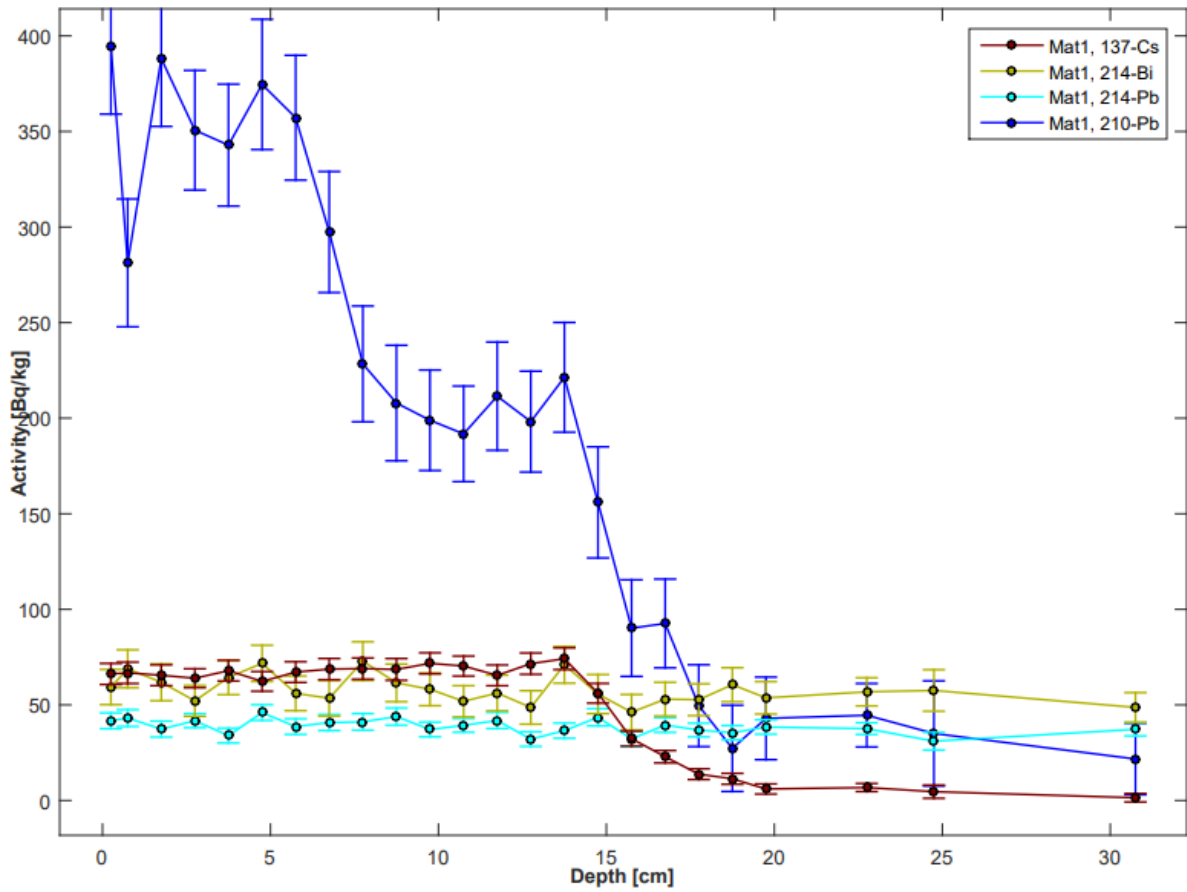


Figure A.4: Mattatall Lake sediment core Activity versus depth plot used to identify the depth at which background  $^{210}\text{Pb}$  concentration is reached.



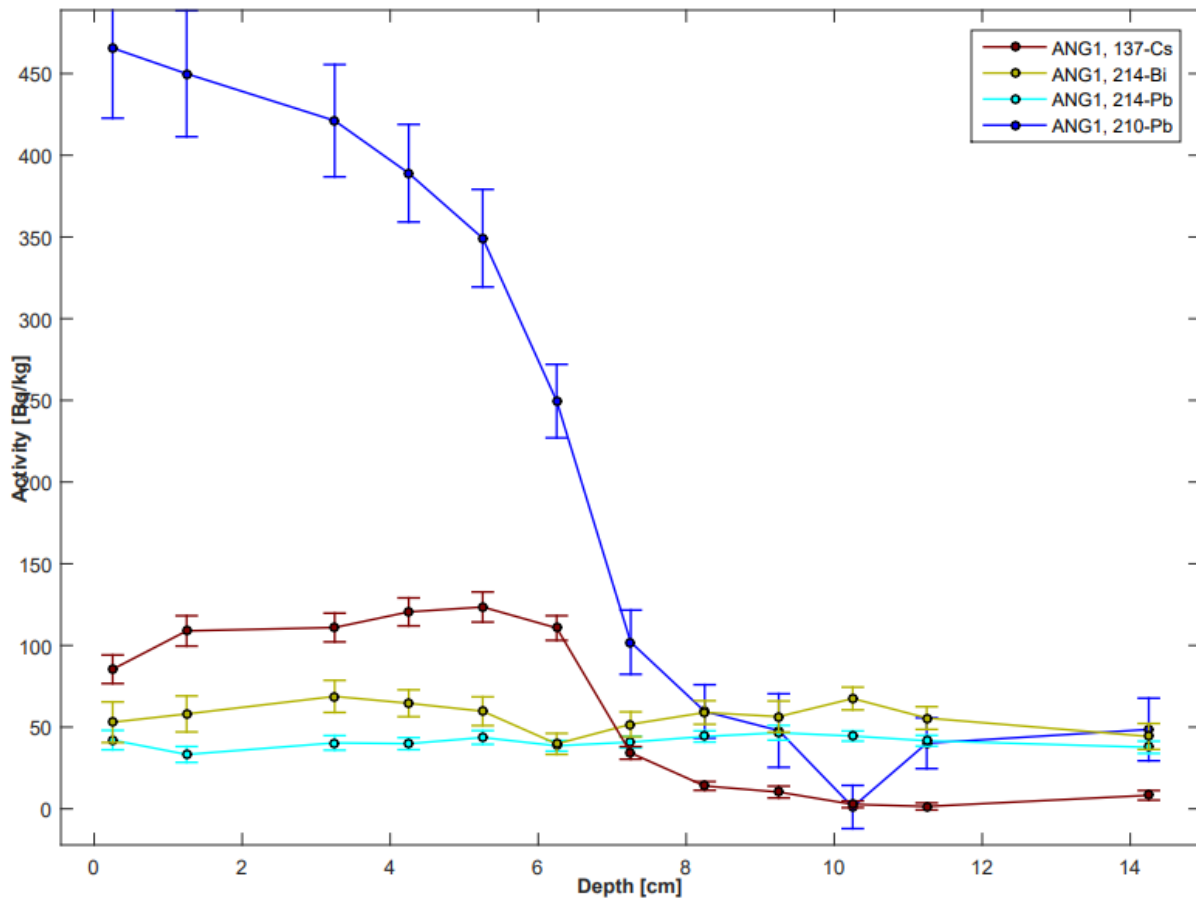


Figure A.5: Angevine Lake sediment core Activity versus depth plot used to identify the depth at which background  $^{210}\text{Pb}$  concentration is reached.