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Ecological and Economic Implications of Increased Storm Frequency and Severity for Boreal Lakes

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**ECOLOGICAL AND ECONOMIC IMPLICATIONS OF INCREASED STORM
FREQUENCY AND SEVERITY FOR BOREAL LAKES**

By

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B.A. Hobart and William Smith Colleges, 2006

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A DISSERTATION

Submitted in Partial Fulfillment of the

Requirements for the Degree of

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(in Ecology and Environmental Science)

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May 2019

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By Kate A. Warner

Dissertation Advisors: Dr. Jasmine E. Saros and Dr. Mario F. Teisl

An Abstract of the Dissertation Presented
in Partial Fulfillment of the Requirements for the
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May 2019

In boreal regions, increased precipitation events have been linked to increased concentrations of dissolved organic carbon (DOC), however less is known about the extent and implications of these events on lakes. We assessed the effects of precipitation events on six drinking water lakes in Maine, USA to better understand how DOC concentration and quality change in response to precipitation events. Our results revealed three types of responses: (1) an initial spike in DOC concentrations and quality metrics; (2) a sustained increase in DOC concentrations and quality metrics and; (3) no change during all sampling periods. Lake residence time was a key driver of changes in DOC concentration and quality. For the same set of drinking water lakes, we investigated a link between changes in DOC to a household's willingness to pay (WTP). Our results revealed that percent change in DOC and SUVA₂₅₄ correspond to initial Secchi depth values. This relationship was used to determine that WTP from improvement in water quality was highest in lakes with shallower Secchi depths and lowest in lakes with deeper Secchi depths. WTP estimates were also correlated with maximum depth, residence time, and percent of wetland coverage. A set of six lakes in Acadia National Park, Maine were evaluated to assess differences in seasonal storm response. Our results revealed

differences in the response of DOC quality metrics to an early summer versus an autumn storm. The response of DOC quality metrics to storms was mediated by differing lake and watershed characteristics as well as seasonal changes in climate such as solar radiation and antecedent weather conditions in the early summer versus autumn.

Investigation of the effects of ice-out timing on physical, biological, and biogeochemical lake characteristics in Arctic and boreal regions during an early and late ice-out regime revealed differences in mixing depths and strength and stability of stratification. Key drivers of observed responses included a combination of climate factors, including solar insolation, air temperature, precipitation, and, in the Arctic, permafrost thaw. This research provides important insights that will be useful for management of water resources as temperature and precipitation patterns continue to change.

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CHAPTER 1

INTRODUCTION

Abrupt climate change (ACC) is defined as rapid changes in Earth's climate or climate events that cause a shift from one environment to another. These shifts can be of variable magnitude, duration, and persistence (National Research Council 2002; Rashid et al. 2011) and include extreme precipitation events. Several definitions of extreme precipitation events persist throughout the literature (Pryor et al. 2009); therefore a uniform consensus to define these events does not exist. Commonly, extreme events are defined by the amount of precipitation within a twenty-four hour period (i.e. Fernandez et al. 2015) or as the top percentile of all rain events that have occurred (i.e. Madsen and Wilcox 2011).

It is widely acknowledged that extreme precipitation events are increasing in many regions across the globe (Grisman et al. 1999; Jentsch et al. 2007). Increased greenhouse gas emissions and warmer temperatures result in increased evaporation, which moistens the air and results in more atmospheric water vapor leading to more intense precipitation events (Karl and Knight 1998; Groisman 1999; Katz 1999; Karl and Trenberth 2003). Due to the location of the Northeastern United States relative to the flow of the jet stream, this portion of the country is susceptible to a greater increase in extreme precipitation than other areas of the country and some regions across the globe (Easterling et al. 2000).

The risks of extreme rain events vary by region, but commonly identified risks include flooding, damage to infrastructure and/or crops and livestock, disruption of transport, potential damage of forests, and water pollution (Madson and Wilcox 2011). Other damages, less commonly identified, include ecological threats to aquatic

ecosystems, which can have subsequent economic effects on water resources such as decreased aesthetic and property values, altered drinking water quality, reduced recreation and tourism, and may lead to negative health effects (Olmstead 2010; Williamson et al. 2017).

Extreme events are receiving extra attention as the frequency and severity of these events continues to increase (Jentsch et al. 2007) therefore, understanding aquatic ecosystem response to these events is important and relevant to current climate trends and concerns. Increased rainfall events may change the water chemistry of lakes, increase concentrations of dissolved organic carbon (DOC) (Klug et al. 2012), lead to nutrient loading, or increase the amount of particulates in the water (Weyhenmeyer et al. 2004). These changes in water chemistry and biology may influence the water clarity or transparency of the lake, including the amount of light available for photosynthesis (Jones et al. 2012), reduce the bioavailability of oxygen and nutrients for organisms in the lake, or alter mixing depth and lake stability (Read and Rose 2013). It is widely acknowledged that frequency and severity of extreme precipitation events has increased, particularly over the last decade (Jentsch et al. 2007), however little is known about the effects of these events on lake ecosystems, drinking water, or on the costs and benefits to communities reliant on these resources.

The primary goal of this research is to investigate how precipitation events affect DOC in aquatic ecosystems and identify potential losses to changes in water quality. DOC has been increasing in many areas of the northern hemisphere and while there are several hypotheses to explain this increase, the growing interest and concerns of extreme precipitation events merit further investigation since the effects of these events on lakes are not clear. These alternative drivers for increasing DOC include reduced sulfate

deposition (Monteith et al. 2007; SanClements et al. 2012), changes in temperature (Freeman et al. 2001; Park and Matzner 2003), and land use change (France et al. 2000). While recent research suggests DOC concentrations increase during wet years (Strock et al. 2016), less is known about the specific ecological effects on lakes. DOC is often regionally and seasonably variable (Sachse et al. 2014) and therefore may change in response to extreme precipitation events. Identifying the role of not only the DOC concentration but also the composition or quality of DOC may elucidate key insights into how the increased DOC may affect aquatic ecosystems. Research conducted for this project would complement the existing literature on changes in DOC and further expand the research by investigating specific ecological effects of extreme events and use an integrated approach to investigate the ecological effects of extreme events in addition to the economic effects.

My research focuses on boreal lakes in the northeastern United States, more specifically in the state of Maine, as this region serves as a good model system due to the increase in frequency and severity of precipitation events, particularly over the past decade. Boreal lakes are the most numerous on Earth (Schindler 1998) and boreal ecosystems are predicted to be one of the biomes most affected by climate change (Ruckstuhl et al. 2008). Additionally, DOC concentrations are expected to increase in boreal lakes by as much as 65% as a result of climate change effects on terrestrial ecosystems (Larson et al. 2011).

The state of Maine is located in the Northeastern U.S. and has approximately 6,000 lakes. Approximately 90% of Maine lakes are drainage lakes, with surface flow into and out of the lakes, while 10% are seepage lakes and are fed by groundwater. Of the 6,000 lakes in Maine, 45 lakes serve as drinking water resources, which provide over half

of the state's drinking water. Lakes are also valuable resources in Maine largely impacting recreation, tourism, and housing costs, all of which are essential to the Maine economy. Precipitation has increased by about six inches in Maine since 1895, especially over the past decade with an increase in extreme precipitation events (Fernandez et al. 2015). Additionally, it is predicted that rainfall will increase by 5-10% between now and 2050, falling in the form of heavy precipitation events (Fernandez et al. 2015). Therefore, increased understanding of how precipitation events impact lake water quality is essential to the state of Maine.

Chapters 2, 3, and 4 investigate the effects of changes in DOC from precipitation events and address ecological implications and economic impacts. The first overarching question is: How do individual storms influence immediate changes in DOC? To address this question, Chapter 2, "Variable responses of dissolved organic carbon to precipitation events in boreal drinking water lakes," focuses on evaluating how DOC concentration and quality differ before and after a precipitation event, and to what extent these changes are sustained over time. The second question is: How do these changes in DOC influence a household's willingness to pay for water quality improvement? Chapter 3, "Can changes in dissolved organic carbon from a rain event be used to estimate willingness to pay for improved water quality?" investigates potential costs to households due to changes in DOC for drinking water resources. The third question is: Does DOC response differ between storms that occur during different times of year? This is addressed in Chapter 4, "Differences in the effects of storms on dissolved organic carbon (DOC) in boreal lakes during an early summer storm and an autumn storm," which investigates changes in DOC during an early summer and an autumn storm. Understanding the

answers to these questions will contribute to literature investigating the effects of changing DOC on aquatic ecosystems.

An additional component of my research includes a collaborative project completed as a trainee in The University of Maine's NSF IGERT program, Adaptation to Abrupt Climate Change. This research explores how changes in the timing of ice out affect arctic versus boreal lake ecosystems. The primary goal of this chapter (Chapter 5) titled, "How Does Changing Ice-Out Affect Arctic versus Boreal Lakes? A Comparison Using Two Years with Ice-Out that Differed by More Than Three Weeks," is to identify how spring and summer lake conditions vary between early and late ice-out years in different regions. More specifically, the goal was to evaluate the effects of ice-out timing on physical, biological, and biogeochemical lake characteristics during an early and late ice-out regime. Widespread changes in the timing of ice-out and the duration of ice cover have been observed throughout the Northern Hemisphere (Kuusisto 1987; Schindler et al. 1990; Livingstone 2000; Magnuson et al. 2000; Futter 2003). These changes, paired with expected future ACC, can lead to important implications for lake ecosystems.

This dissertation explores the impact of ACC on aquatic ecosystems, with a primary focus on ecological implications of increased DOC from precipitation events, and secondarily, economic costs associated with changing DOC. As temperature and precipitation patterns continue to change, aquatic ecosystems will also change which could have large implications for water quality and the communities reliant on these resources. This thesis provides information to better evaluate lake characteristics to identify aquatic resources that may be more vulnerable to change, and conceptual frameworks to better visualize changes in DOC occurring as a result of precipitation events.

CHAPTER 2

VARIABLE RESPONSES OF DISSOLVED ORGANIC CARBON TO PRECIPITATION EVENTS IN BOREAL DRINKING WATER LAKES

2.1. Abstract

In boreal regions, increased concentrations of dissolved organic carbon (DOC) have been linked to extreme wet years; however, less is known about the extent to which precipitation events are altering DOC concentration and quality. We assessed the effects of rain events on a suite of six lakes in Maine, U.S.A., to better understand how events alter DOC quantity and quality. DOC concentrations and DOC quality (measured as DOC-specific absorption coefficients (Specific Ultraviolet Absorbance (SUVA₂₅₄ (also a^*_{254}), a^*_{320} , and a^*_{380})) were quantified 24 hours before, and at three time points (24-48 hours, 5-7 days, and 3 weeks) after five different precipitation events. Our results revealed three types of responses across the lakes: (1) an initial spike in DOC concentrations of 30-133% and in the three quality metrics of 20-86% compared to pre-storm levels, followed by return to pre-storm concentrations; (2) a sustained increase in DOC concentrations (by 4-23%) and an increase in the three DOC quality metrics (by 1-43%) through the second post-storm sampling, with concentrations falling by the third post-storm sampling compared to pre-storm levels; and (3) no change during all sampling periods. Lake residence time was a key driver of changes in DOC concentration and DOC quality, and the watershed area:lake area ratio was also an important variable in determining lake response to storm events. Our research provides evidence that precipitation events contribute to short-term abrupt changes in DOC quantity and quality that are largely driven by key landscape and lake characteristics. These changes in DOC

may have important implications for management of water utilities, including alteration or implementation of treatment strategies.

2.2. Introduction

The frequency and severity of extreme precipitation events are increasing across many regions (Groisman et al. 1999; Jentsch et al. 2007; Donat et al. 2013; Easterling et al. 2017). These events may exert a stronger effect on ecosystems than gradual climate change (Huber and Gullede 2011), and the frequency and severity of these events is predicted to continue to increase (Jentsch et al. 2007). The location of the northeastern US relative to the flow of the jet stream makes this area more susceptible to increases in extreme precipitation than other areas of the US and some regions across the globe (Easterling et al. 2000). Indeed, since 1950, the region has experienced a 70% increase in extreme precipitation events (Madsen and Figdor 2007; Spierre et al. 2010; Madsen and Wilcox 2011; Melillo et al. 2014; Frei et al. 2015; Huang et al. 2017; Huang et al. 2018), the highest percent increase in the country.

In boreal regions, one of the key concerns with higher rainfall is an increase in the amount of dissolved organic carbon (DOC) that flows into lakes and streams. DOC is largely derived from terrestrial sources (McKnight et al. 2003; Prairie 2008; Burns et al. 2016), and enters aquatic ecosystems via surface, ground, and soil waters (Moore 2003; Roulet and Moore 2006). Modification in transport by run-off from the watershed to lakes and streams from changes in precipitation intensity, frequency, and duration may contribute to elevated levels of DOC (Delpla et al. 2009; Whitehead et al. 2009). DOC concentrations are expected to increase in boreal lakes by as much as 65% by the end of the century as a result of climate change effects on terrestrial ecosystems (Larson et al. 2011). This could have harmful effects on the chemical and biological quality of boreal

aquatic ecosystems and drinking water (Delpla et al. 2009; Roig et al. 2011). DOC plays a key role in determining water transparency, mixing depth, oxygen availability, and the bioavailability and processing of nutrients and toxic compounds in lakes (Williamson et al. 1999). Additionally, rising DOC concentrations in water supplies contribute to harmful by-products and increased levels of complexed heavy metals and adsorbed organic pollutants (Matilainen 2010). Clearly, the increased frequency and severity of precipitation events and subsequent increases in DOC are a key concern for drinking water quality in boreal lakes.

Landscape features in boreal regions also contribute to elevated DOC concentrations within lakes, and these features can further modulate the effects of precipitation events. For example, DOC concentration and quality are related to the watershed area:lake area ratio (WA:LA) (Schindler 1971; Xenopoulos et al. 2003) and are influenced by wetlands (Dillon and Malot 1997; Temnerud et al. 2014) and forested landscapes in the watershed (Nguyen et al. 2013; Chen et al. 2016). Higher precipitation increases the amount and rate of stream, groundwater, and subsurface inflows into lakes (Lee et al. 2007); thus, these landscape features may contribute to the flushing of large amounts of DOC from upper soil horizons of watersheds into lakes (Hinton et al. 1997). The lake residence time can also alter the influx and processing of DOC in the lake (Xenopoulos et al. 2003). Consideration of key landscape features surrounding lakes is important in assessing the impacts of rainfall and subsequent changes in DOC.

Recent studies suggest links between increased DOC concentrations in surface waters and higher precipitation at various time scales. An analysis of a 30-year database of surface water geochemistry and watershed-specific landscape data for 84 remote lakes throughout the Northeast suggests that during extreme wet years, lake DOC concentration

increases (Strock et al. 2016). In Lake Mälaren, Sweden, a higher color and increased DOC concentration have been associated with extreme precipitation events (Weyhenmeyer et al. 2004). In this lake, DOC increased by 26% when color increased from 20 to 35 mg Pt L⁻¹. Both of these studies demonstrate links between DOC concentration and precipitation at annual time scales. Over shorter time scales, Jennings et al. (2012) evaluated changes in seven lakes for 13 weather-related episodic events and found increases in DOC over a monthly time period in response to precipitation. Williamson et al. (2014) evaluated key DOC quality variables to identify lake response to climate and found that these variables all had significant responses to precipitation within 30 to 75 days, the majority of lakes showing the largest responses between 60 and 75 days. This work suggests that evaluating lake response to changes in certain DOC variables over a longer time period may be important in observing maximum change. In contrast, Raymond et al. (2016) used models to evaluate event-based delivery of DOC from major hydrologic events and suggested that individual events account for a large percentage of annual terrestrial DOC input to streams. This model suggests important changes in DOC likely occur over days, supporting the need for further monitoring of the effects of precipitation on DOC at short timescales. The immediate changes in DOC concentration and quality that occur within a day or a week after a precipitation event remain unclear.

To address the extent to which precipitation events affect boreal drinking water lakes requires a better understanding of the effects of individual storm events on drinking water sources. How do DOC concentration and quality differ before and after a precipitation event, and to what extent are any changes sustained over time? To improve understanding of the influence of precipitation events and subsequent changes in DOC on

boreal drinking water lakes, we selected six lakes in Maine, USA, to evaluate changes in the DOC concentration and quality metrics before and after five storm events. Samples at each lake were collected 24-48 hours before the storm, and 24-48 hours, 5-7 days, and 3-4 weeks after the storm event. Additionally, we evaluated changes in phytoplankton community structure for one storm event to investigate possible associated biological changes from a precipitation event.

2.3. Methods

2.3.1. Site description and lake selection

The state of Maine is located in the Northeastern U.S. and contains approximately 6,000 lakes. Bedrock across the state of Maine varies, with northern Maine's bedrock largely comprised of metamorphic rocks such as gneiss and schist, while southern, coastal, and western Maine contains large areas of granite, and central Maine is comprised of sedimentary rocks with large amounts of carbonate. Of the approximately 6,000 lakes, 45 are used as drinking water resources that provide roughly half of the State's drinking water (www.maine.gov/dhhs/mecdc/environmental-health/dwp/consumers/surfaceWater.shtml). Six of the 45 lakes in Maine that serve as drinking water resources were selected for this study (Figure 2.1). Lakes were selected based on morphometric and baseline chemical data collected during prior sampling seasons (Table 2.1). We chose lakes that varied in size and volume as well as WA:LA to account for potential landscape effects (e.g., the influence of wetlands on DOC concentrations and quality). Lake sizes, measured in area, ranged from 0.1 to 121.4 km², and lake volume ranged from 0.2 x10⁶ to 3,977 x10⁶ m³. DOC concentrations for the six selected lakes ranged from less than 2 mg L⁻¹ in Jordan Pond to almost 5 mg L⁻¹ in

Nokomis Pond (Table 2.1). The variation in lake features allowed us to investigate how storms affected different types of aquatic ecosystems.

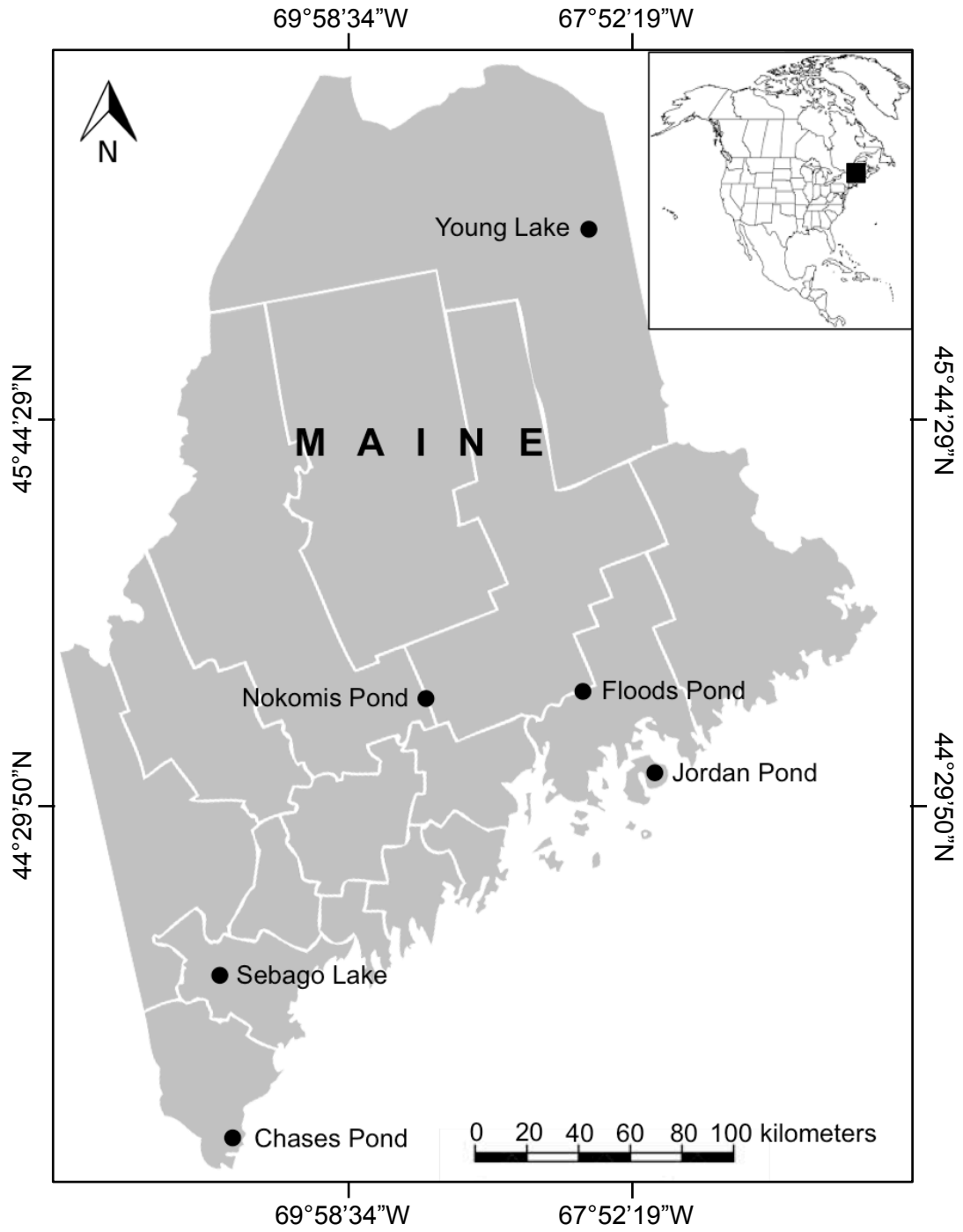


Figure 2.1. Location of the 6 selected study lakes across the State of Maine.

Table 2.1. Select morphometric and chemical characteristics of the 6 selected drinking water lakes.

Drinking Water Source	Watershed Area (km²)	Lake Area (km²)	Volume (x10⁶ m³)	Max Depth (m)	Mean Secchi (m)	Mean DOC (mg L⁻¹)	Mean Chl <i>a</i> (µg L⁻¹)
Young Lake	1.5	0.1	0.2	2.5	2.5*	3.3	6.2
Floods Pond	11.2	2.6	32	45	9.0	3.5	2.8
Nokomis Pond	3.1	0.8	2.2	7	4.3	4.6	6.6
Chases Pond	10.0	0.5	1.7	11	6.8	2.7	4.9
Jordan Pond	4.0	0.8	17	45	12.5	1.7	1.3
Sebago Lake	457.7	121.0	3977	96	10.0	2.5	1.6

*Secchi depth measurement ends at bottom of lake

2.3.2. Collection of storm water samples

On average, over the past several decades, the northeastern U.S. has experienced at least 7 events annually with at least 25 mm of rain falling over a 24-hour period (Spierre et al. 2010). By evaluating these events with 25 mm of rain over a 24-hour period, pertinent water quality information can be provided to drinking water utilities. Storm water samples were collected from the intake whenever a rain event was predicted between mid May and mid November. Five storms were evaluated in this study from Fall 2015 to Fall 2016 (Table 2.2). Precipitation data were collected from the closest weather station to each lake (Table 2.2). Every lake did not receive 25 mm of precipitation for all events. A plot representing the total rainfall from September 1, 2015 to October 31, 2016 collected from a weather station near one of the study lakes shows the size of the rain events compared to all precipitation events (including snow) throughout the duration of

the study (Figure 2.2). Additional information on the amounts of rainfall before and during sampling periods can be found in Appendix A.

Samples were collected at each of the six study lakes 24 hours before (Pre), 24-48 hours after (P1), 5-7 days after (P2), and 3-4 weeks after the precipitation events (P3). For each of the six lakes, the corresponding water district collected samples from the intake inside the pump house or water treatment plant for each sampling period (Pre, P1, P2, and P3). Only raw (i.e., not treated) water samples were collected for analysis. One opaque 1-L pre-rinsed acid washed bottle for analysis of DOC, total phosphorus (TP), total nitrogen (TN), nitrate (NO_3^-), and ammonium (NH_4^+) and one brown 1-L pre-rinsed soap-washed bottle for analysis of chlorophyll *a* and phytoplankton community structure were filled during each of the Pre, P1, P2, and P3 sampling periods. Each 1-L bottle was rinsed three times with lake intake water, then filled, capped, and stored in a cool dark place until shipping. After collection of the Pre, P1, and P2 samples, bottles were shipped overnight to the University of Maine for analysis. P3 samples were shipped upon collection and were not collected for Storm 3 or for Storm 5. Upon receipt of samples, each was filtered as necessary and separated into bottles for analysis of water quality metrics. More detailed methods and results for nutrient and chlorophyll *a* analyses can be found in Appendix A.

Table 2.2. Dates of the five storms and the amount of rainfall at each of the 6 lakes. Rainfall amounts are in mm. Weather station indicates where rainfall data were collected from.

Drinking Water Source	Weather Station	<i>Storm 1</i>	<i>Storm 2</i>	<i>Storm 3</i>	<i>Storm 4</i>	<i>Storm 5</i>
		Sept. 30, 2015	Oct. 28, 2015	Nov. 19, 2015	June 5, 2016	Oct. 21, 2016
Young Lake	Northern Maine Regional at Presque Isle Station	45.2	29.7	25.4	15.2	30.7
Floods Pond	Bangor International Airport Station	139.2	38.4	23.1	18.0	33.5
Nokomis Pond	Bangor International Airport Station	139.2	38.4	23.1	18.0	33.5
Chases Pond	Pease International Tradeport Station	71.6	45.0	27.2	31.2	80.5
Jordan Pond	Acadia National Park McFarland Hill Weather Station	84.1	62.5	23.1	25.9	30.2
Sebago Lake	Portland International Airport Station	149.9	40.1	37.3	61.7	108.5

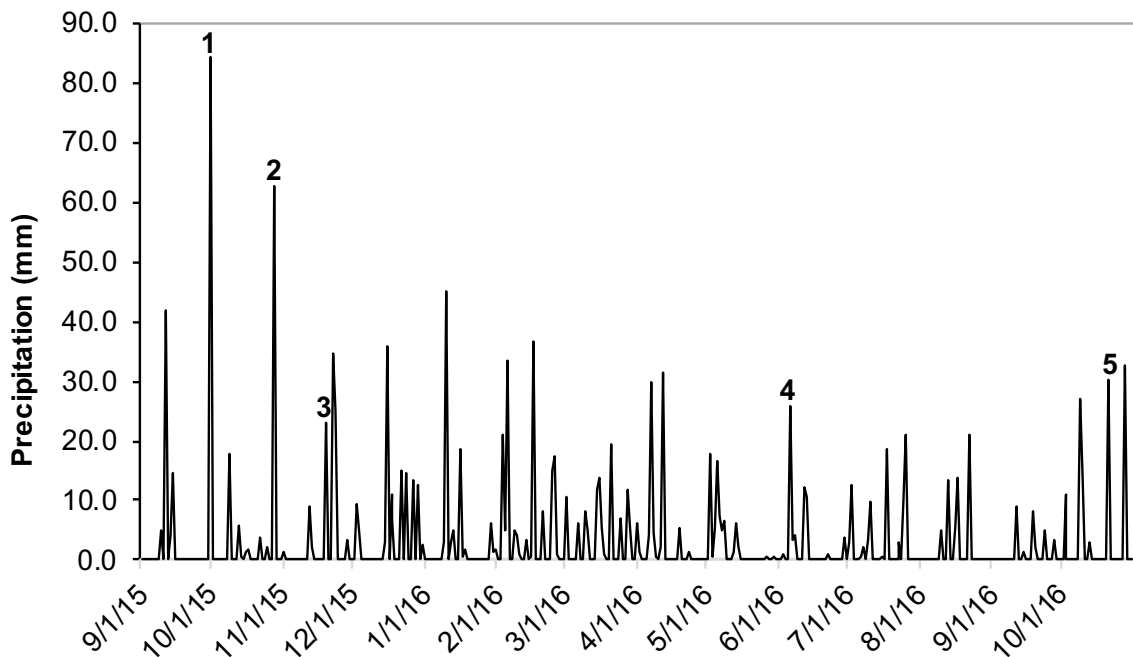


Figure 2.2. Total daily precipitation in mm for Acadia National Park (Jordan Pond) from September 1, 2015 to October 31, 2016. Number corresponds to storm event.

2.3.3. Analysis of DOC concentration and absorbance properties

All storm samples were analyzed for DOC concentration and quality immediately upon receipt. DOC samples were filtered through 25 mm Whatman GF/F filters pre-rinsed with deionized water. DOC concentrations were analyzed on a Shimadzu Total Organic Carbon Analyzer. DOC quality was assessed by measuring the absorbance properties within 200-800 nm wavelengths using a Varian Cary UV-VIS spectrophotometer. A Milli-Q deionized water blank was subtracted from the raw absorbance values to provide corrected absorbance values. Napierian dissolved absorption coefficients were calculated using the following equation (Helms et al. 2008; Kirk 2011):

$$a_d = \frac{2.303 \times D}{r}$$

where D is the decadal optical density value from the spectrophotometer and r (measured in meters) is the path length of the quartz cuvette. DOC-specific absorption coefficients

(Specific Ultraviolet Absorbance ($SUVA_{254}$ (also a^*_{254}), a^*_{320} , and a^*_{380}) and spectral slopes were calculated to evaluate DOC quality. $SUVA_{254}$, a^*_{320} , and a^*_{380} were calculated by dividing a_d by the DOC concentration (mg L^{-1}). Changes in $SUVA_{254}$ are used by many drinking water utilities to assess the aromaticity or reactivity of DOC in water, which contributes to determining the amount of chemicals used for treatment (Nguyen et al. 2013). Changes in a^*_{320} and a^*_{380} can give insights into the source and chemical properties of the DOC that aids in assessing drinking water and monitoring biogeochemical trends (Jaffe et al. 2008). Changes in DOC composition or quality are variable across lakes, providing an effective way to evaluate how different lakes may respond to precipitation events.

Relative Response (RR) of DOC concentrations, $SUVA_{254}$, a^*_{320} , and a^*_{380} was also calculated. P1, P2, and P3 samples were each normalized to the Pre sample: $RR = (\text{PostX} / \text{Pre}) - 1$, where x is the Post1, Post2, or Post3. RR values less than zero indicate a decrease in that parameter, positive values indicate an increase, and zero indicates no change.

To calculate spectral slopes over the 275-295 nm range ($S_{275-295}$), linear regression was used to estimate the slope of the relationship between $\ln a_d$ and wavelength, expressed as a positive number. Following Williamson et al. (2014), DOC-related climate forcing optical indices (CF) were calculated using the ratio, $a^*_{320} : S_{275-295}$; larger numbers are indicative of wetter and cooler conditions. For each sampling period (Pre, P1, P2, P3), a^*_{320} and $S_{275-295}$ were each averaged across the five storms. CF gives insight into the relationship between precipitation and temperature dependence of DOC concentrations (Williamson et al. 2014) These indices reveal that DOC quality might be

more responsive to precipitation events than DOC quantity (Helms et al. 2008; Williamson et al. 2014).

2.3.4. Comparison of lake surface water and intake samples

To determine if samples collected from the intake were representative of the lake, we collected surface water samples in the middle of the lake at some of the sites on the same or similar day that samples were collected from the intake (Table 2.3). Samples were collected in the opaque and brown 1-L bottles, the same as collection from the intake, and identical analyses were performed using the same methods. More detailed methods, and results, for nutrient and chlorophyll *a* analyses for lake and intake comparisons can be found in Appendix A.

Table 2.3. Comparison of samples taken from lake surface water and the intake on the same or similar days.

Drinking Water Source	Date	Source	DOC (mg L⁻¹)	SUVA₂₅₄ (L mg-C⁻¹ m⁻¹)	<i>a</i>^{*320} (L mg-C⁻¹ m⁻¹)	<i>a</i>^{*380} (L mg-C⁻¹ m⁻¹)
Floods Pond	8/11/15	lake intake	3.5	7.0	2.4	0.9
Jordan Pond	10/7/15	lake intake	1.9	4.8	1.4	0.5
	10/6/15	lake intake	1.9	4.7	1.5	0.6
	10/22/15	lake intake	1.8	5.0	1.5	0.5
	10/20/15	lake intake	1.7	4.9	1.5	0.5
Chases Pond	10/20/15	lake intake	2.5	5.6	1.9	0.7
	10/20/15	lake intake	2.6	5.1	1.7	0.6
Nokomis Pond	11/3/15	lake intake	5.3	7.6	2.8	1.1
	11/3/15	lake intake	5.3	7.5	2.8	1.1

2.3.5. Landscape/watershed data

Landscape and lake morphometry data for each lake were collected from the Lakes of Maine website (www.lakesofmaine.org), which archives data from the Maine Department of Environmental Protection, Maine Inland Fisheries and Wildlife, and the Maine Office of GIS. Specific data collected included WA:LA, as well as the percent impervious cover, agriculture, and developed areas in the watershed (Table 2.4). Additional land cover data, including percent mixed forest and scrub-shrub, were collected using 2011 National Gap Analysis Land Cover data from the United States Geological Survey (Table 2.4). The average slope of the watershed was calculated using digital elevation models collected from the Maine Office of GIS (Table 2.4). Percent wetland coverage in the watershed was calculated using the United States Fish and Wildlife Service Wetlands Mapper (www.fws.gov/wetlands/data.mapper.html; Table 4). Residence time was calculated as the inverse of the flushing rate, which was measured as times per year (Table 2.4). Many of the lake and landscape variables in this study varied across the six lakes. WA:LA ranged from 3.9 for Nokomis Pond to 20 for Chases Pond, residence time ranged from 0.2 to 6.7 years, and total percent wetland ranged from 2% to 80% of the watershed area (Table 2.4). The slope was also variable across the six lakes ranging from 6.7 degrees at Sebago lake to 47.5 degrees at Jordan Pond (Table 2.4). Mixed forest cover dominates the watersheds of most lakes with the exception of Young Lake that is predominantly covered by wetland (Table 2.4). The type of forest cover is similar across most lakes. Qualitative analysis of Maine vegetation suggests Young Lake and Nokomis Pond have slightly more deciduous cover and equal percent coverage of coniferous and mixed forests, Jordan Pond has more coniferous cover and equal percent coverage of deciduous and mixed forest, and Floods Pond, Chases Pond, and Sebago

Lake have equal percent coverage of deciduous, coniferous, and mixed forest cover. The percent coverage of agricultural land, impervious cover, and developed areas within the lake watersheds were relatively similar (Table 2.4)

Table 2.4. Lake and landscape variables for each of the 6 study lakes. WA:LA is the ratio of watershed area to lake area and percentages indicate the percent cover found in the watershed.

Drinking Water Source	WA:LA	Residence Time (years)	Slope (degrees)	% Landcover						
				Mixed Forest	Scrub-Shrub	Forest/Shrub Wetland	Freshwater Emergent Wetland	Agricultural	Impervious Cover	Developed
Young Lake	15	0.2	35.2	20	0	70	10	0	0	0
Floods Pond	4.3	2.6	13.7	97	0	2	0	0	0.2	0.8
Nokomis Pond	3.9	1.2	23.7	60	0	24	1	8	1.9	5.1
Chases Pond	20	0.3	7.8	74	3	13	4	1	1.0	4.0
Jordan Pond	5.0	5.9	47.5	64	24	2	1	0	1.4	7.6
Sebago Lake	3.8	6.7	6.7	77	2	7	1	1	1.0	11.0

2.3.6. Phytoplankton community composition

Two 50-ml centrifuge tubes for Pre and P2 samples from each lake were filled with unfiltered water from the 1-L brown bottles for analysis of phytoplankton. Pre and P2 samples from the September 30, 2015 storm were counted to evaluate changes in phytoplankton community before and after a precipitation event. This storm was selected for phytoplankton analysis because it was the largest precipitation event sampled. Samples were preserved with Lugol's solution, settled in Utermohl chambers and counted using a Nikon Eclipse TS-100 inverted microscope at 400X magnification. A minimum of 300 individuals was counted to genus or species level as possible for each sample. Phytoplankton counts were converted to biovolume by measuring the dimensions of 20 or more individuals and determining the average biovolume of each taxon using the closest geometric shape (Wetzel and Likens 2000). Biovolume data were then grouped into major algal phyla.

2.3.7. Data analysis

To assess if the sampling period or the storm event affected DOC collectively across all lakes, a linear mixed effects model was used for the DOC metrics. Data were log transformed to meet assumptions of constant variance and normality and relationships where $p < 0.05$ were considered significant.

Within each lake, we assessed whether storms altered the DOC concentrations, $SUVA_{254}$, a^*_{320} , and a^*_{380} , and if any changes were sustained by using a randomized block design to conduct a repeated measures Analysis of Variance (ANOVA) test. Rain events were treated as blocks, and Pre, P1, and P2 were the treatments. A significance level of $p < 0.05$ was used and the Greenhouse-Geiser correction was used to test for the assumption of sphericity. Post-hoc analysis was conducted using a Bonferroni correction.

This test evaluated differences before and after all storm events for each lake and also identified whether or not any changes were sustained.

To evaluate if Storms 1 through 5 resulted in different responses within each lake, a one-way ANOVA was used to compare the mean DOC concentrations and DOC quality metrics of all sampling periods for each storm. This allowed us to evaluate if storms with different precipitation amounts or at different times of year influenced the DOC response. A significance level of $p < 0.05$ was used and Levene's test for homogeneity and Shapiro-Wilks normality test were used to test for the assumptions of ANOVA. To determine which means were significantly different from one another, Tukey's honestly significant differences post-hoc test was used.

To compare Pre and P2 samples for phytoplankton biovolume in each lake, a one-way ANOVA with a Tukey's post-hoc test was used to assess differences between major taxa before and after the storm event, as well as a test for significant differences in major taxa within each the Pre and P2 samples individually. A significance level of $p < 0.05$ was used.

Simple linear regression was used to assess whether WA:LA, residence time, slope, or total percent wetland coverage affected the mean percent change in DOC concentration, $SUVA_{254}$, and a^*_{320} to storms. Mean percent change is the average percent change between Pre storm samples and the P2 storm samples (collected six days after the precipitation event) for each lake. Relationships where $p < 0.05$ were considered significant. All statistical analyses were conducted using R software (version 3.3.2, The R Foundation for Statistical Computing, 2016).

2.4. Results

2.4.1. Precipitation events at each study site

The amount of precipitation was greatest for Storm 1 across all sites except at Chases Pond, where Storm 5 was the largest (Table 2.2). Storm 1 was the second largest storm for Chases Pond. Storm 3 or Storm 4 had the least amount of precipitation across all sites (Table 2.2). For a few events, not all sites received at least 25 mm of precipitation. Floods Pond, Nokomis Pond, and Jordan Pond received < 25 mm of precipitation during Storm 3, and Young Lake, Floods Pond, Nokomis Pond, and Jordan Pond received < 25 mm of precipitation for Storm 4 (Table 2.2).

2.4.2. Response of DOC metrics across all lakes to storm event and period sampled

When assessed collectively across all six lakes, DOC concentration differed between sampling periods and storms ($p < 0.05$), but there was no interactive effect between the period sampled and the storm (Table 2.5). DOC concentration increased from the Pre to the P1 sampling period, and DOC concentrations were different across the lakes for each of the five storms ($p < 0.05$). For $SUVA_{254}$ and a^*_{320} , there were no significant effects of the period sampled, the storm event, or the interactive effect between them. Across all lakes, however, a^*_{380} was either collectively higher or lower during different storms ($p < 0.05$; Table 2.5).

Table 2.5. Results of linear mixed model to assess effects of period sampled and storm across all lakes, with p-values indicated for each test.

	DOC (mg L⁻¹)	SUVA₂₅₄ (L mg-C⁻¹ m⁻¹)	<i>a</i>^{*320} (L mg-C⁻¹ m⁻¹)	<i>a</i>^{*380} (L mg-C⁻¹ m⁻¹)
Period	0.04 ^a	0.13	0.13	0.31
Storm	0.02 ^a	0.23	0.06	0.02 ^a
Period x Storm	0.92	0.85	0.97	0.95

^aThe sampling period or the storm has a significant effect on DOC concentration or quality among all lakes.

2.4.3. Relative response of DOC metrics within each lake to storm events

The RR of DOC concentrations varied across lakes and storm events (Figure 2.3), with three response patterns emerging among lakes. An immediate, relatively large, but short-lived increase occurred in Young Lake. DOC concentrations spiked during P1 sampling, followed by an immediate decrease by P2. Young Lake RR for P1 ranged from 0.30 for Storm 4 to 1.33 for Storm 1 (Figure 2.3). A gradual, moderate and sometimes sustained increase occurred in Floods and Nokomis Ponds. On average across all storms, the RR of DOC increased from the Pre to the P1 sampling and again from the P1 to the P2 sampling. The change in RR for the five storms in these lakes ranged from 0 to 0.17 for the Pre to P1 sampling and from 0 to 0.23 for the Pre to P2 sampling (Figure 2.3). Little or no change occurred in Chases Pond, Jordan Pond, and Sebago Lake. These lakes had the lowest RR values for all storms and showed little or no change between Pre, P1, and P2 samplings, with the RR response for these periods across the three lakes ranging from -0.04 to 0.09 (Figure 2.3). The RR for P3 was variable across all lakes, typically decreasing to or below Pre storm values (Figure 2.3). Generally, the largest RR values occurred for the largest storm at each site (Storm 1 for all lakes except Chases Pond, where Storm 5 was the largest) (Figure 2.3).

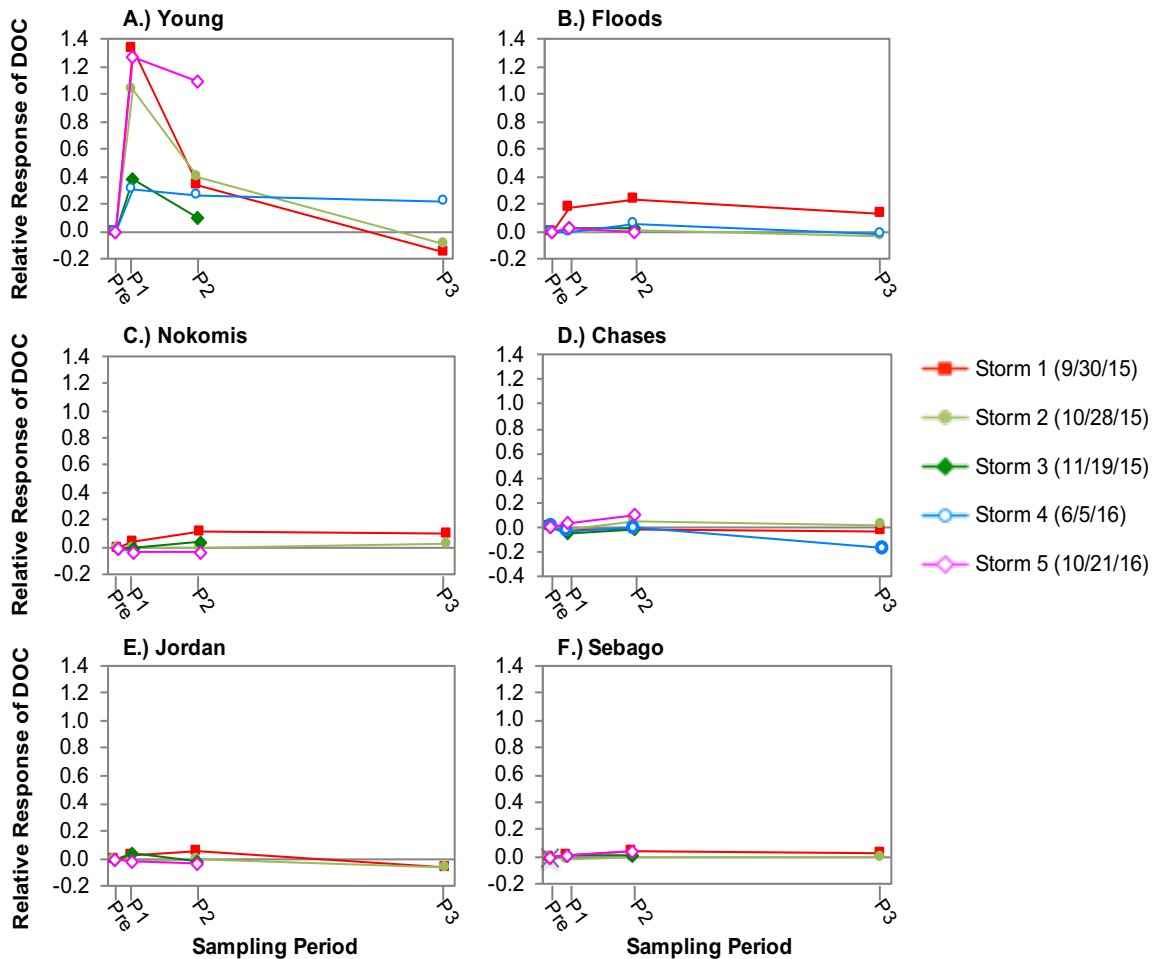


Figure 2.3. Relative response of DOC concentration to precipitation events. Relative responses for the five storms are expressed as P1, P2, or P3 compared to Pre. Lakes are plotted in order of DOC response, Young Lake having the largest response and Sebago Lake having the smallest.

Responses of DOC quality metrics ($SUVA_{254}$, a^*_{320} , and a^*_{380}) were more variable in each lake compared to DOC concentrations for both the sampling period and storm. While there was more variability, particularly in the response of each lake to the different storm events, similar patterns to the DOC concentration responses emerged for the DOC quality metrics (Figure 2.4). Young Lake again had a relatively large but short-lived increase in the RR of the DOC quality metrics. The three metrics spiked during P1 sampling, followed by a decrease by P2. RR from Pre to P1 ranged from 0.02 to 0.37 for $SUVA_{254}$, 0.06 to 0.72 for a^*_{320} , and 0.07 to 0.86 for a^*_{380} . In Floods and Nokomis Ponds a gradual and sometimes sustained increase in all metrics occurred. Similar to DOC concentration, on average across all storms, the RR of all DOC metrics increased from the Pre to the P1 sampling and again from the P1 to the P2 sampling. RR in Floods Pond from Pre to P2 ranged from -0.07 to 0.07 for $SUVA_{254}$, -0.03 to 0.16 for a^*_{320} , and -0.04 to 0.20 for a^*_{380} . RR in Nokomis Pond from Pre to P2 ranged from 0.01 to 0.11 for $SUVA_{254}$, 0.01 to 0.27 for a^*_{320} , and 0.01 to 0.43 for a^*_{380} (Figure 2.4). Chases Pond, Jordan Pond, and Sebago Lake were variable and either increased or decreased from Pre to P1 or P2 (Figure 2.4). Little change occurred in Chases Pond, except during Storm 5, where RR from Pre to P1 increased by 0.17 for $SUVA_{254}$, by 0.35 for a^*_{320} , and by 0.45 for a^*_{380} (Figure 2.4). In Jordan Pond, from Pre to P1, the three DOC quality metrics increased during Storms 2 and 3, and decreased during Storms 1 and 5 followed by a return toward Pre storm levels during P2 (Figure 2.4). Little or no change in RR occurred in Sebago Lake (Figure 2.4). Young Lake, Floods Pond, and Nokomis Pond had the highest RR during Storm 1 for all three quality metrics, similar to the DOC response (Figure 2.4).

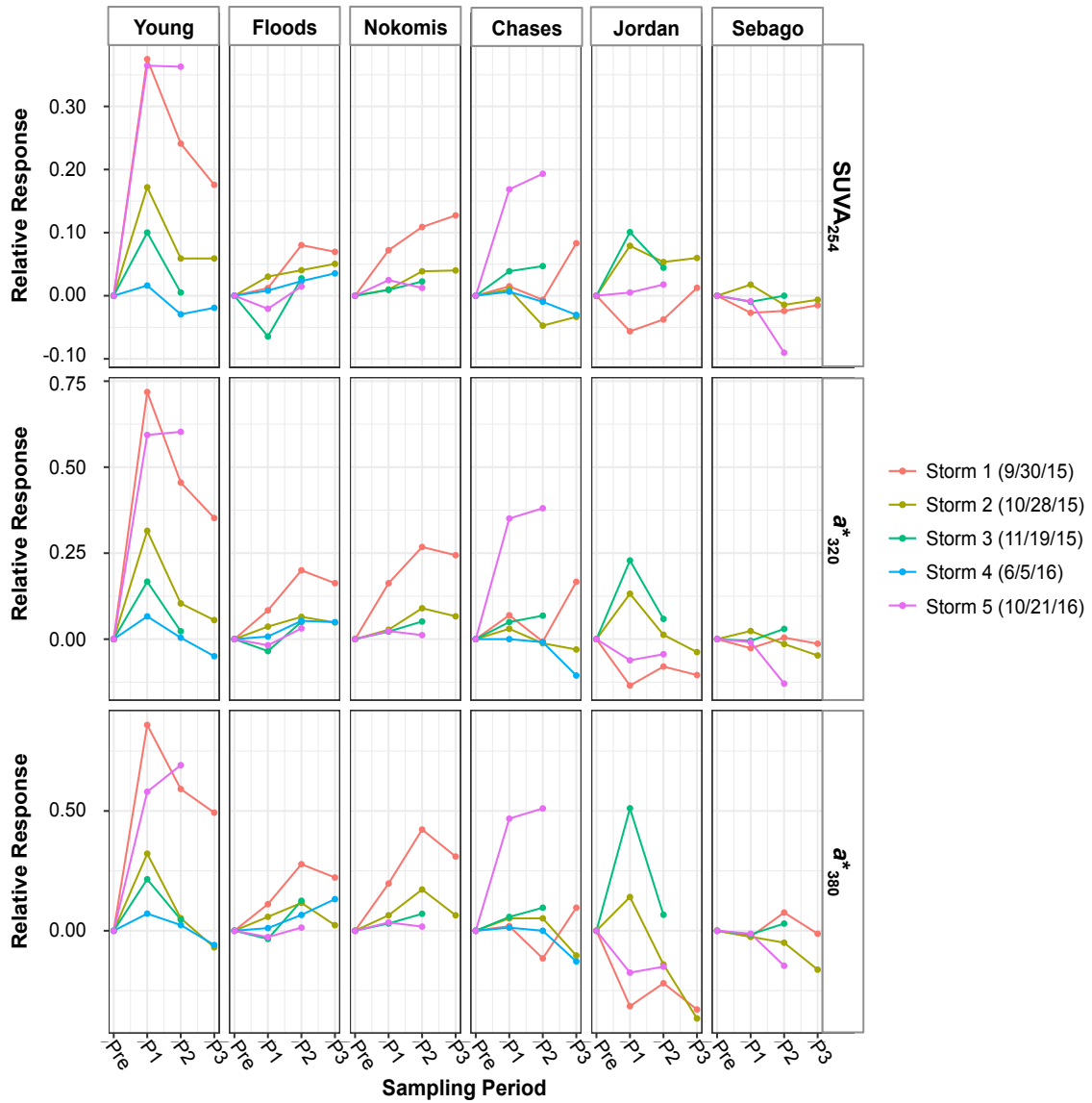


Figure 2.4. Relative response of SUVA₂₅₄, a*₃₂₀, and a*₃₈₀ to precipitation events. Relative responses for the 5 storms are expressed as values at sampling periods P1, P2, and P3 compared to Pre. Lakes are plotted in order of DOC response, Young Lake having the largest response and Sebago Lake having the smallest.

2.4.4. Effect of period and storm event within each lake

Young Lake was the only lake in which the timing of sampling, or the period, had a significant effect on DOC response; however, storm event did not have a significant effect. This reflects the consistently positive response of all DOC metrics at P1 after all storms. Young Lake was highly responsive to precipitation; DOC concentration ($p < 0.05$), SUVA₂₅₄, and a^*_{320} , increased from Pre to P1 ($p < 0.10$). This is in contrast to the other five lakes in which the sampling period had no significant effect, but the magnitude of the DOC response varied across storms. Floods and Nokomis Ponds demonstrated a few similar patterns of RR in DOC concentration and quality metrics. In Floods Pond, DOC concentration for all sampling periods were higher during Storm 1 compared to Storms 2, 4, and 5 ($p < 0.05$). In Nokomis Pond, the response of DOC concentration was higher during Storm 1 compared to Storm 5 ($p < 0.05$). There were no significant differences for DOC quality metrics in Floods or Nokomis Ponds. The response of DOC concentration during storm events in Chases Pond, Jordan Pond, and Sebago Lake were not significantly different ($p > 0.05$), and quality metrics varied slightly. In Chases Pond, Storm 5 quality metrics were higher compared to Storm 4 ($p < 0.05$). In Jordan Pond, for all DOC quality metrics, Storm 3 values were higher than Storm 1 ($p < 0.05$). In Sebago Lake, there were no significant differences across all DOC metrics ($p > 0.05$).

2.4.5. Climate forcing optical index

The mean response (mean \pm standard error) of the CF index for each sampling period averaged across all of the storms resulted in the same three patterns that emerged from the RR of DOC concentration, with the exception of Chases Pond (Figure 2.5). In Young Lake, the CF index spiked from Pre to P1 and immediately decreased by P2 and sustained the decrease by P3. The CF indices were 143 ± 17 during the Pre storm period,

230 ± 21 by P1, 197 ± 16 by P2, and 159 ± 21 by P3 (Figure 2.5). In Young Lake this was a significant response ($p < 0.05$) and had the highest R^2 value of 0.96 (Figure 2.5). Again, a gradual, moderate and sometimes sustained increase occurred in Floods and Nokomis Ponds. Floods Pond CF indices ranged from 128 ± 8 during the Pre storm period to 143 ± 5 by P3 (Figure 2.5). Nokomis Pond CF indices ranged from 117 ± 17 during the Pre storm period to 141 ± 7 by P3 (Figure 2.5). Chases Pond responded similarly to Young Lake, with an increase in the CF index from Pre to P1 and a decrease thereafter. The CF indices in Chases Pond were 86 ± 12 for Pre storm, 96 ± 9 for P1, 94 ± 10 for P2, and 91 ± 7 for P3 (Figure 2.5). The CF index for Jordan Pond decreased from 72 ± 9 during Pre storm conditions to 61 ± 8 by P3, the opposite of Young Lake, Floods Pond, and Nokomis Pond (Figure 2.5). Sebago Lake had little to no change in the CF indices.

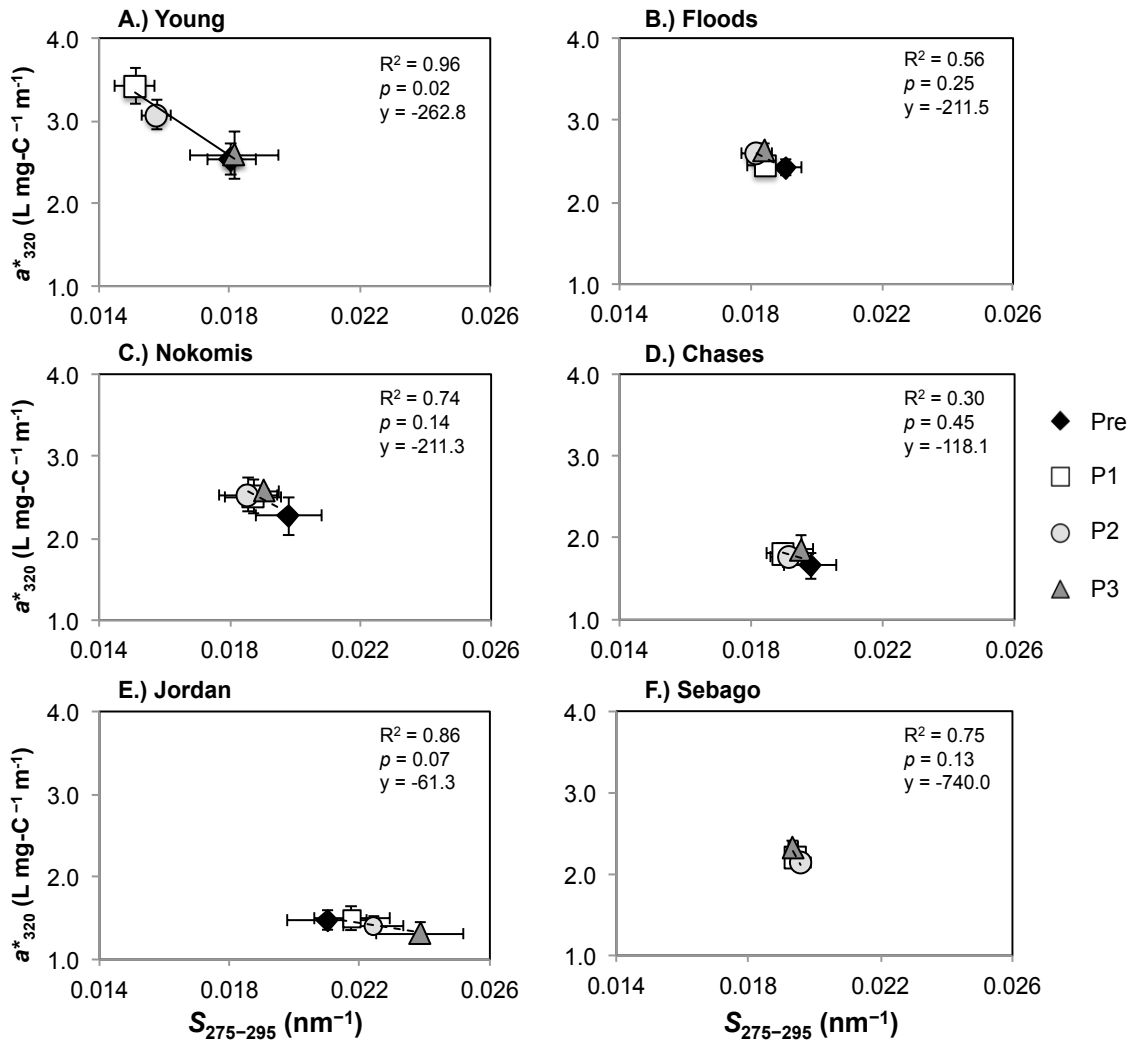


Figure 2.5. Climate forcing optical index (CF index) values from precipitation events. Pre, P1, P2, and P3 samplings are averaged across the five precipitation events (\pm standard error) for each of the six study lakes. Bars indicate standard error. Dashed lines are regression lines.

2.4.6. Relationship between lake and landscape variables and DOC metrics

Percent wetland coverage in the watershed was positively correlated with mean percent change in DOC, mean percent change in $SUVA_{254}$, and mean percent change in a^*_{320} ($p < 0.05$; Figure 2.6), however this relationship is driven by Young Lake.

Residence time had a negative effect on the mean percent change in a^*_{320} ($p < 0.05$).

Mean percent change in DOC and mean percent change in $SUVA_{254}$ also had negative slopes; however, they were not significant (Figure 2.6). There were no significant relationships between mean percent change in DOC, $SUVA_{254}$, or a^*_{320} with respect to WA:LA (Figure 2.6). There were no significant relationships between slope and percent change in DOC ($p = 0.53$), $SUVA_{254}$ ($p = 0.39$), or a^*_{320} ($p = 0.74$).

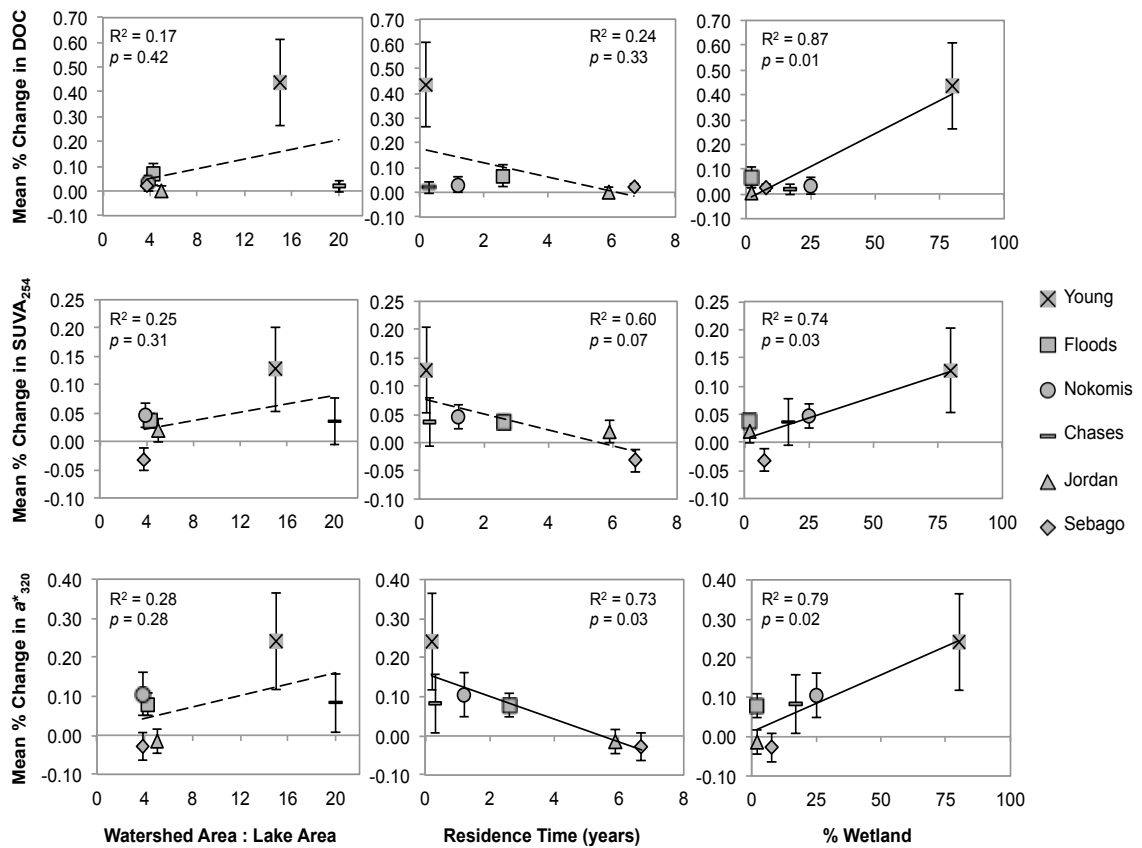


Figure 2.6. Relationships between DOC metrics and landscape variables. Relationships across the 6 study lakes between are the mean percent change in DOC, SUVA₂₅₄, or *a**₃₂₀ (\pm standard error) and the ratio of watershed area to lake area, residence time (measured in years), or percent wetland in the watershed. Values for each lake are averaged across the 5 storms. Percent change was calculated from pre-storm to the second post storm collection, 5-7 days after the storm events. Bars indicate standard error. Significant trends are indicated by solid lines.

2.4.7. Phytoplankton community composition

In general, total phytoplankton biovolume was highest in Young Lake, lower in Floods and Nokomis Ponds, and lowest in Chases Pond, Jordan Pond, and Sebago Lake. Total biovolume was higher during the Pre storm period in Young Lake ($p < 0.01$). In contrast, although only significant in Nokomis Pond ($p < 0.05$), total biovolume was higher during the P2 period for the five other lakes. Overall there were no significant differences for each specific phytoplankton phylum within each lake between Pre and P2 periods (e.g., diatom Pre compared to diatom P2), with the exception of Young Lake which had more chrysophytes during the Pre storm period ($p < 0.05$; Figure 2.7), and Nokomis and Jordan ponds, which had more chrysophytes during the P2 period ($p < 0.01$; Figure 2.7).

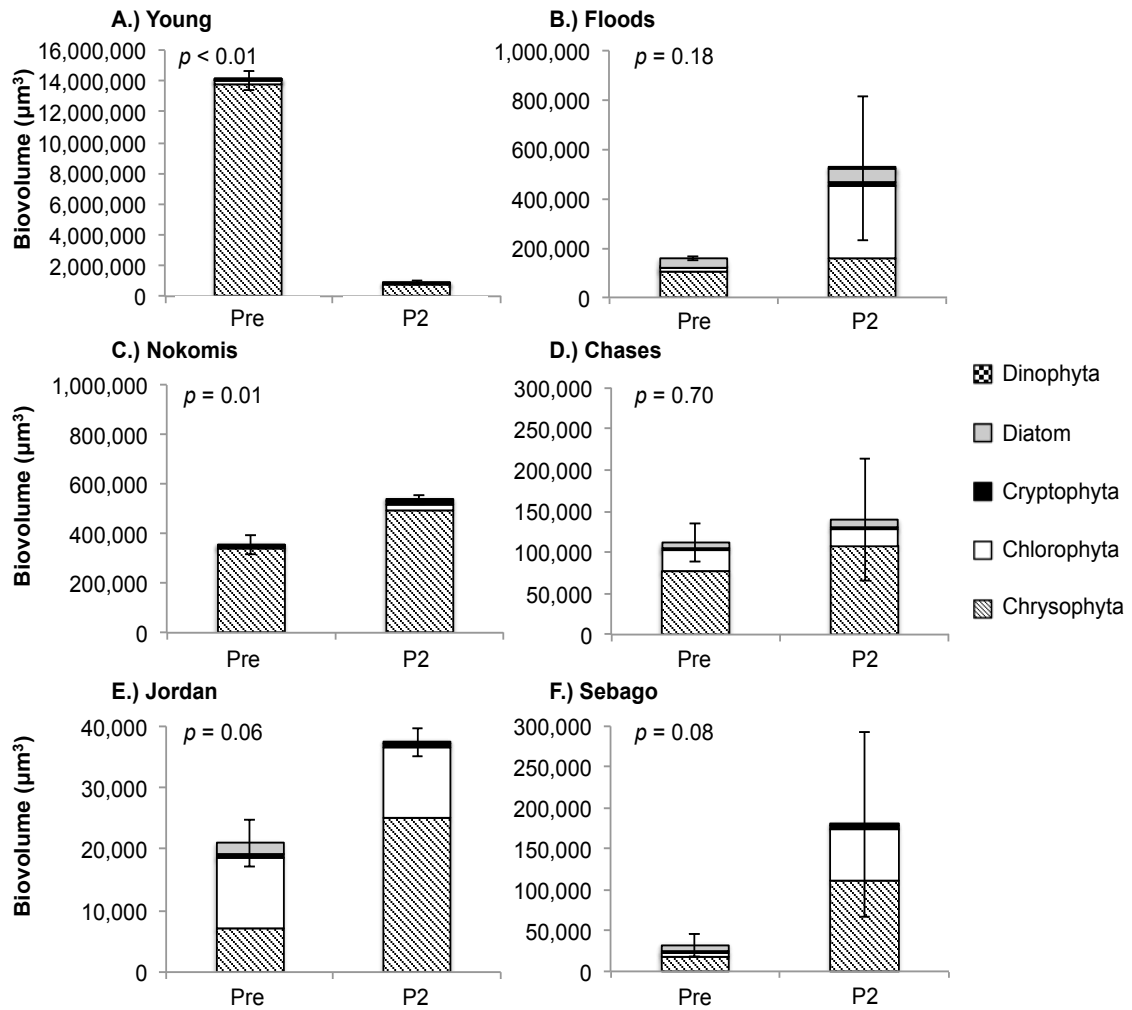


Figure 2.7. Absolute biovolume between Pre and P2 for the September 30, 2015 storm. Pre samples were collected 24-48 hours prior to the precipitation event and P2 samples were collected 5-7 days after the storm event. Note the change of scale on the y-axes across plots. P values reflect comparisons between total Pre and P2 biovolume for each lake.

2.5. Discussion

Our results suggest that the role of precipitation events in controlling lake DOC concentration and quality varies among lakes, with the strength and duration of the response to these events shaped by landscape and lake morphometric features. Three patterns of DOC response emerged from the lakes in our study (Figure 2.8), with each of the lakes falling into one of the following three categories: 1) a spike in DOC concentration and $SUVA_{254}$, a^*_{320} , and a^*_{380} values immediately after a storm event, followed by a rapid return to Pre storm conditions; 2) a gradual and sometimes sustained increase in DOC concentration and $SUVA_{254}$, a^*_{320} , and a^*_{380} values; and 3) little to no change in DOC concentrations with variable responses in $SUVA_{254}$, a^*_{320} , and a^*_{380} values. Residence time plays a key role in determining the type of response each lake will exhibit. This information provides important insights to help water managers assess the potential implications of future storm events. While water treatment processes and methods vary, utilities face common challenges from rain events, and appropriate management responses are likely to vary with landscape and lake morphometric features.

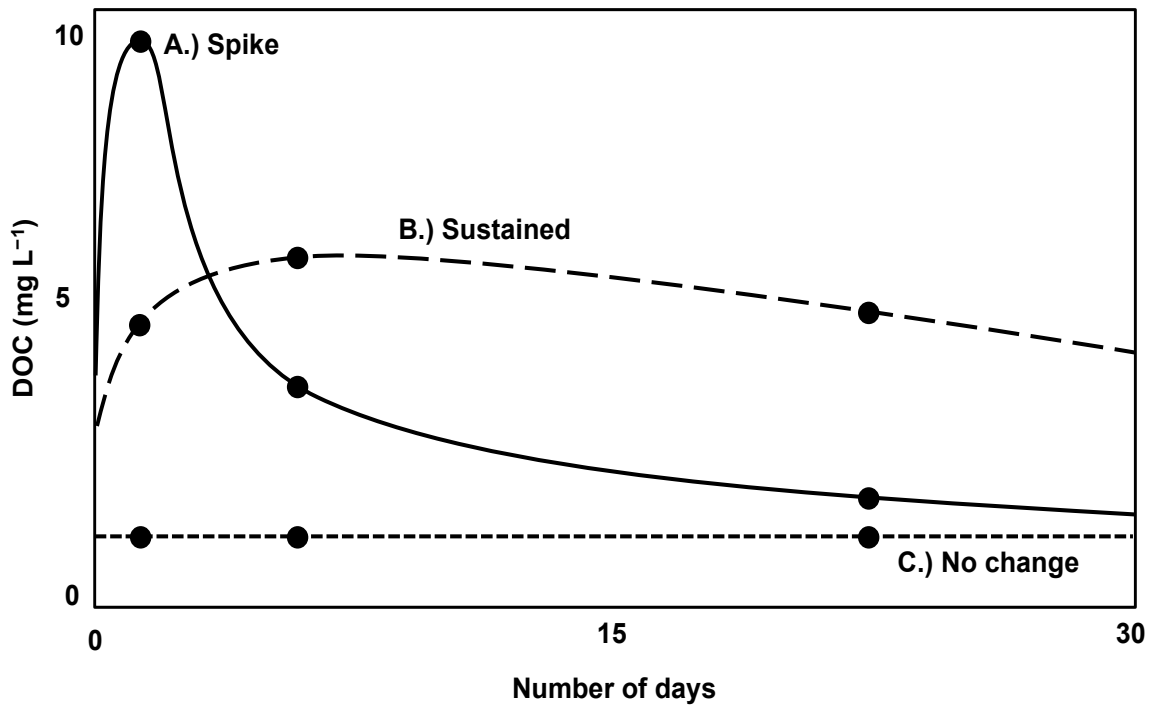


Figure 2.8. Conceptual diagram of the three DOC response patterns from precipitation events, A.) Spike, B.) Sustained, and C.) No change. Dots indicate values at P1, P2, and P3 sample collection. Pre storm values are at time 0.

The spike pattern in DOC concentration and quality is predominantly attributed to short residence time. The response of DOC in Young Lake is indicative of a rapid delivery of water into the lake and a rapid exit. In Young Lake, DOC concentration, $SUVA_{254}$, a^*_{320} , and a^*_{380} respond very similarly to one another supporting the importance of short residence time as a driver of changes in this system. Precipitation events could exacerbate effects of short residence time in lake ecosystems, as increased runoff from the events may lead to even shorter water residence time and the increased flows increase DOC concentrations at various time points (Tranvik et al. 2009). Drinking water utilities using lakes that exhibit rapid increases in DOC concentrations with precipitation events may need to make strong temporary adjustments to treatment strategies, such as increases in select chemicals used to treat the particular water resource.

The second observed pattern of a moderate, sometimes sustained increase in DOC concentrations, $SUVA_{254}$, a^*_{320} , and a^*_{380} results from moderate (1-2 year) residence times in which the DOC is being retained for a period. Floods Pond and Nokomis Pond have varying lake depths and volumes; however, they have several similarities that are important drivers of observed change in DOC from precipitation events. These include similar residence times, WA:LA ratios, and initial DOC concentrations. DOC flowing into lakes and streams from precipitation events is likely terrestrially derived (Curtis and Schindler 1997). DOC concentrations typically increase with increasing catchment size (Inamdar and Mitchell 2006), thus the similar response of Floods and Nokomis Ponds may be attributed to the similar WA:LA ratios as well as similar initial DOC concentrations, which are higher than those of other lakes in this study. Therefore, these similarities between the two lakes suggest that residence time and WA:LA are the key drivers of the sustained DOC response to precipitation events. Compared to lakes with the spike pattern, lakes that exhibit a pattern of sustained increase in DOC may require milder treatments but for a longer period of time or could prompt alterations to treatment facilities. These management responses include temporarily less costly adaptations such as increased addition of chemicals (i.e., aluminum or ferric salts), or longer term, and initially more expensive, treatment options such as installation of an ozone treatment system.

The third pattern of little to no change in DOC concentration and variable responses in $SUVA_{254}$, a^*_{320} , and a^*_{380} results from several factors; while these lakes exhibited similar responses, the landscape and lake morphometric attributes contributing to any change varied. Chases Pond has a relatively high WA:LA ratio and a short residence time, which is suggestive of larger DOC fluctuations. Chases Pond has several

inflows where a pulse of DOC may be detected; however, this may alter the DOC quality more than the concentration (Hruska et al. 2001; Hood et al. 2006), which is evident in the greater variability of DOC quality in Chases Pond. Jordan Pond and Sebago Lake have some similar landscape and morphometric features. They are both deep, clear lakes with low baseline DOC concentrations and longer residence times compared to the other lakes in this study. These features and the large volume of these lakes likely contribute to the minimal change in DOC during precipitation events. Similar to Chases Pond, changes in $SUVA_{254}$, a^*_{320} , and a^*_{380} in Jordan Pond and Sebago Lake are more variable than the changes in DOC concentration. Changes in quality are also important for water quality managers to monitor, as for example, increases in $SUVA_{254}$ often indicate more aromatic carbon (Weishaar et al. 2003; Fu et al. 2006) which is often less bioavailable in lakes (Perdue 1998). $SUVA_{254}$ and other UV absorbance values are important for identifying the quality of DOC and also the treatability of the drinking water (Ritson et al. 2014), thus monitoring changes in water quality following weather events is an important consideration for water management authorities.

We have attributed several important distinctions among lake response to landscape features, importantly percentage of wetlands in the watershed and lake residence time. This relationship between residence time and the mean percent change in DOC concentration, $SUVA_{254}$, and a^*_{320} is a strong predictor variable in understanding DOC response. Relationships have previously been documented between DOC concentration and quality and wetlands (Kortelainen 1993; Dillon and Molot 1997; Gergel et al. 1999). While we note a strong relationship with the percent wetland and the mean percent change in DOC concentration, $SUVA_{254}$, and a^*_{320} , it is important to note that this relationship is strongly driven by the large extent of wetlands around and large

change in DOC concentration in Young Lake. Young Lake and Nokomis Pond have larger percentages of wetlands than the other lakes, which could also be contributing to the higher DOC concentrations. While residence time and WA:LA are the main drivers of DOC change in Floods Pond, it is possible that hidden or cryptic wetlands may influence the fluctuations in DOC concentration and the quality of the DOC. Cryptic wetlands are areas of the watershed that have low slope and may have inundated soils but there is no visible wetland habitat on the surface (Winn et al. 2009), they are hidden under forest canopy and can be large contributors to DOC export from forested catchments (Creed et al. 2003). Additionally, it is important to acknowledge that there has been significant research that discusses the importance of within lake processes contributing to loss of DOC (Bertilsson and Tranvik 2000; von Wachenfeldt et al. 2008). Based on the residence times of Floods and Nokomis Ponds, however, these processes are not rapid enough for the loss of DOC through in-lake processes to be more than the inflow of terrestrial DOC (Canham et al. 2004). It is difficult to discern specific drivers of DOC change; wetlands appear to be a strong predictor however this response is driven by the response of Young Lake; thus residence time is the strongest predictor of changes in DOC concentration and quality from precipitation events in this study.

The same three patterns emerged when evaluating the CF index compared to the DOC responses, and the residence time and WA:LA modify how lakes plot along these climate indices. The CF index is most responsive in the lakes with larger WA:LA ratios and shorter residence times, and DOC inputs have little influence on the lakes with smaller WA:LA ratios and longer residence times, suggesting that photobleaching is dominant. The CF index evaluates lake response across timescales (Williamson et al. 2014), and these indices can tell us about the source of the DOC and the subsequent

quality. For example, DOC with a lower $S_{275-295}$ and higher a^*_{320} is typically terrestrially derived and more colored and less bioavailable (Helms et al. 2008), which may influence photosynthesis or aquatic food webs (Jones et al. 2012), and have further implications. UV absorbance and DOC have been used as indicators of the presence of organic matter in drinking water (Thomas and Burgess 2007). The CF index allows for evaluation of ecosystem changes across lakes, which could support decisions regarding adaptations or revisions to existing management strategies.

A consequence of these fluctuations in DOC concentration, $SUVA_{254}$, a^*_{320} , and a^*_{320} , from precipitation events is changes in the phytoplankton community. The same landscape and lake morphometric features also influence phytoplankton response. Additionally, other physical and chemical properties of the lakes may be altered by storms, importantly nutrients among others (i.e. pH, temperature, dissolved oxygen). Although not statistically significant among all lakes, the observed changes in phytoplankton could still have important ecological implications. DOC provides additional carbon sources directly and indirectly by stimulating heterotrophic bacterial growth, thereby influencing phytoplankton community structure of mixotrophic algae, including chrysophytes (Xenopoulos et al. 2009). Changes in DOC due to storms can affect the quantity and quality of light that is available for phytoplankton (Philips et al. 2000). In most of the study lakes, the biovolume of chrysophytes may have increased because chrysophytes are mobile and can stay elevated in the water column (Reynolds 1984) allowing them to outcompete other types of phytoplankton after storm events. In Young Lake, the rapid rate of flushing likely contributed to the decrease in overall biovolume from Pre to P2. Water temperature and the timing of turnover are also important factors that may contribute to changes in phytoplankton, as well as nutrient

concentrations. Nutrients can increase from storm events and influence phytoplankton communities (Padisák et al. 1988), however in the set of lakes we examined, nutrients did not change in response to the storm events (see Appendix A). With respect to characteristics and water quality metrics measured in this study, changes in DOC and residence time are likely key factors contributing to changes in phytoplankton phyla, and are important considerations for future precipitation events and drinking water. Changes in algae from storm events have important implications for drinking water treatment as algae can be one of the contributors to disinfection by-products (DBPs), in particular haloacetic acids (Chen et al. 2008)

Over the course of this study, samples from only one spring storm were collected compared to four from fall storms. This may affect DOC response; however, while DOC concentration may fluctuate seasonally, research suggests that the seasonal variability is minor relative to the variability among lakes (Gergel et al. 1999). Seasonal effects on DOC quality warrant further research. Our research underscores the complexity of changes in DOC concentrations and quality during precipitation events and gives insight into patterns of change that persist across lake and landscape types, thus establishing a baseline for implications to water treatment systems, and for establishing adaptive management strategies. Fulvic and humic constituents of DOC are important precursors for DBPs (Rook 1974), such as the trihalomethanes (THMs), which have carcinogenic effects (Christman et al. 1990). DOC in drinking water that is treated by alum or iron is directly related to the THM formation potential (van Leeuwen et al. 2005; Uyak and Toroz 2007). Further, allochthonous DOC flowing into drinking water resources from storm events can contribute to increased DBPs when oxidized (Pagano et al. 2014). These

relationships suggest water treatments will likely need to be altered with increasing DOC from precipitation events.

2.6. Conclusion

Three key patterns emerged from the results of our study, an immediate spike, a sustained increase, and no change in DOC concentrations in response to precipitation events. These same patterns were evident in the response of $SUVA_{254}$, a^*_{320} , and a^*_{380} , with increased variability for the lakes in which DOC concentrations did not change. Residence time was a key driver of the observed changes, and WA:LA was also an important variable in determining lake response. Identifying these patterns and evaluating DOC quality metrics in addition to DOC concentration will be critical for monitoring, modifying, and adapting management strategies in light of these events. This study provides key insights to preemptively alter management strategies to ensure consistent, high water quality for drinking water resources as precipitation events are predicted to continue to increase in frequency and severity.

CHAPTER 3

ECOLOGICAL AND ECONOMIC IMPLICATIONS OF PRECIPITATION EVENTS ON MAINE'S DRINKING WATER RESOURCES: LINKING CHANGES IN DISSOLVED ORGANIC CARBON TO WELFARE IMPACTS FROM CHANGING WATER QUALITY

3.1 Abstract

Increases in precipitation events are associated with increasing concentrations of dissolved organic carbon (DOC). However, less is known about the implications of such increases for water quality and the welfare impacts of these changes in water quality. We evaluated DOC and Specific Ultraviolet Absorbance (SUVA₂₅₄) for a set of Maine lakes to reveal how changes in DOC and SUVA₂₅₄ from precipitation events might influence Secchi depths, and, in turn impact welfare estimates. Our results revealed relationships between initial Secchi depth values and percent change in DOC and SUVA₂₅₄. Estimated losses from changes in water clarity were highest in lakes with Secchi depths from 2 to 4 meters and lowest in lakes with Secchi depths deeper than 6 meters. Estimated losses were also correlated with the maximum depth of the lake, residence time, percent of wetland coverage, and DOC and SUVA₂₅₄. Our research provides evidence that changes in DOC and SUVA₂₅₄ from storm events correspond to changes in Secchi depth and contribute to losses per household. These relationships are mediated by lake and watershed variables. This research provides an important, cost-effective management tool for water utilities to assess losses that may result from future increases in precipitation events and subsequent increases in DOC.

3.2 Introduction

Precipitation events have increased in many regions across the globe (Groisman et al. 1999; Jentsch et al. 2008; Donat et al. 2013; Easterling et al. 2017), particularly in the northeastern United States, with a 60-70 percent increase since the 1950s (Madsen and Figdor 2007; Spierre et al. 2010; Madsen and Wilcox 2011; Melillo et al. 2014; Frei et al., 2015; Huang et al. 2017; Huang et al. 2018). These changes in precipitation could have important implications on drinking water resources, altering water quality and the cost of treating and providing drinking water. In addition, decreased water quality can impose other types of costs on communities such as loss of property value and decreased recreation experiences, among others. Evaluating the impacts of rain events on drinking water sources in a region where the impacts may be large is useful for guiding regional assessment of both the ecological and economic implications of changes in precipitation on drinking water resources.

Extreme precipitation events are receiving extra attention as the frequency and severity of these events continues to increase (Jentsch et al. 2007). Therefore, understanding aquatic ecosystem response to these events is important. Increased rainfall events may change the water chemistry of drinking water lakes, including increases in concentrations of dissolved organic carbon (DOC) (Klug et al. 2012). DOC is largely derived from the terrestrial environment and commonly results from the decomposition of plant and animal material on the landscape; DOC becomes dissolved in water, and flows into lakes and streams through surface, ground, and soil waters (Moore 2003; Roulet & Moore 2006). DOC is essential to ecosystem structure and function (Williamson et al. 1999; Couture et al. 2012) and plays a key role in determining water transparency (Williamson et al. 1999). Current research suggests links between long-term

increases in DOC and declines in water transparency (Strock et al. 2017). DOC concentrations are expected to increase in boreal lakes by as much as 65% as a result of climate change effects, including increases in precipitation, on terrestrial ecosystems (Larson et al. 2011). Further understanding of the effects of precipitation on drinking water resources and potential losses to communities will be important for management of drinking water resources.

Increasing DOC and its resultant biological effects have potentially important implications for drinking water quality. Algal blooms of a certain colonial species contribute to taste and odor problems in drinking water sources (Nicholls and Gerrath 1985; Nicholls 1995). Harmful by-products and increased levels of complexed heavy metals and adsorbed organic pollutants are additional problems created by a rise in DOC concentrations in drinking water (Matilainen 2010). Increased DOC concentrations have been associated with extreme precipitation events in other locations including Lake Mälaren, Sweden. Results from a 15-year study on Lake Mälaren suggest that when DOC concentrations are higher, water treatment costs increase significantly (Ledesma et al. 2012). Fewer studies report how Specific Ultraviolet Absorbance (known as SUVA₂₅₄) responds to storm events in lakes. SUVA₂₅₄ is commonly known as a “quality” metric of DOC, in other words, it can indicate the source of DOC or provide insight as to the structure of the DOC (Weishaar et al. 2003). SUVA₂₅₄ is commonly measured by water treatment managers to indicate how much of a certain chemical (e.g. chlorine or bromine) should be added to drinking water (Nguyen et al. 2013) and can be an indicator of potential harmful by-product formation (Park et al. 2019). The state of Maine, located in the northeastern U.S., is well situated to investigate increases in DOC and changes in SUVA₂₅₄ and to serve as a model for areas experiencing increased precipitation events.

These precipitation events, and subsequent increases in DOC may increase water treatment costs and impose other economic losses (lost property tax revenues, lost economic activity) on communities. Drinking water utilities are growing concerned as increases in DOC may correlate with increases in disinfection by-products (DBP's) (Van Leeuwen et al. 2005; Uyak and Toroz 2007), which can have health implications (Plewa & Wagner 2009; Richardson et al. 2007). Some drinking water utilities in Maine have already observed changes in DOC in recent decades and Maine drinking water utilities already monitor for several chemicals, including disinfection by-products (DWP Annual Compliance Report 2017). Additional monitoring of DOC and SUVA₂₅₄ may be able to aid in management of drinking water sources.

Understanding relationships between ecological changes and possible economic changes is also useful for management. Information on water quality value, in particular identifying links between changes in water quality and changes in management, is increasingly demanded by decisions makers (Kinzig et al. 2011). Water quality is valued highly by the public, however there is no generalized framework for linking changes in water quality to changes in economic costs or benefits (Keeler et al. 2012). Valuing changes in water quality is challenging as the costs and benefits of such changes vary across individuals and by spatial and temporal scales. Therefore multiple frameworks or methods may need to be created depending on the region and potential drivers of water quality change. Integrating ecological observations with economic analyses is an important first step for identifying changes in value related to changes in drinking water resources.

To identify the ecological and economic implications of increased precipitation on Maine's drinking water sources requires a better understanding of changes in DOC from

storm events on individual lakes, including how changing DOC may change water quality and a method to translate these changes into potential losses or gains associated with changing water quality. How might changes in DOC correlate with losses per household? To investigate this question, we (1) identified key lake and watershed metrics related to DOC and SUVA₂₅₄ concentrations across 12 Maine lakes; (2) quantified immediate changes in DOC concentration and SUVA₂₅₄ in 6 drinking water lakes from precipitation events pre- and post-storm; and (3) estimated the welfare impacts of potential changes to water quality using a function transfer based on a meta-analysis conducted by Ge et al. (2013), quantifying immediate and long-term losses.

3.3. Methods

3.3.1 Site description and lake selection

The state of Maine is located in the Northeastern U.S. and is home to approximately 6,000 lakes. Of the 6,000 lakes, 45 are used as drinking water resources and provide half of the state's drinking water. Based on a set of ecological and economic criteria, we selected twelve of the 45 lakes in Maine that serve as drinking water resources for this research (Figure 3.1; Table 3.1). These 12 lakes provided baseline data for further storm analysis. The lakes served a range of populations from about 300 people to 140,000 people. Lake sizes ranged from 0.1 km² to 121.4 km² and DOC concentrations for the 12 selected lakes ranged from less than 2 mg L⁻¹ in Jordan Pond to almost 7 mg L⁻¹ in Big Wood Pond.

Out of the 12 lakes selected to complete initial evaluation of lake characteristics, six lakes were chosen to investigate storm response based on the initial baseline chemical data as well as location, demographics, and the size of the population served (Figure 3.1; Table 3.1). The representative six lakes were distributed across the state of Maine to

account for differences in climate and precipitation. Variation in lake size and volume across the six lakes allowed us to investigate how water resources of varying sizes responded to storm events and understand how losses differed. Surrounding landscape, including wetlands, impervious cover and land uses, were also assessed to identify potentially important watershed features that affected response to storm events. The surrounding populations were of varying size and economic status. We accounted for water sources that serve a large portion of Maine's population and also controlled for variation in resources to implement adaptation strategies.

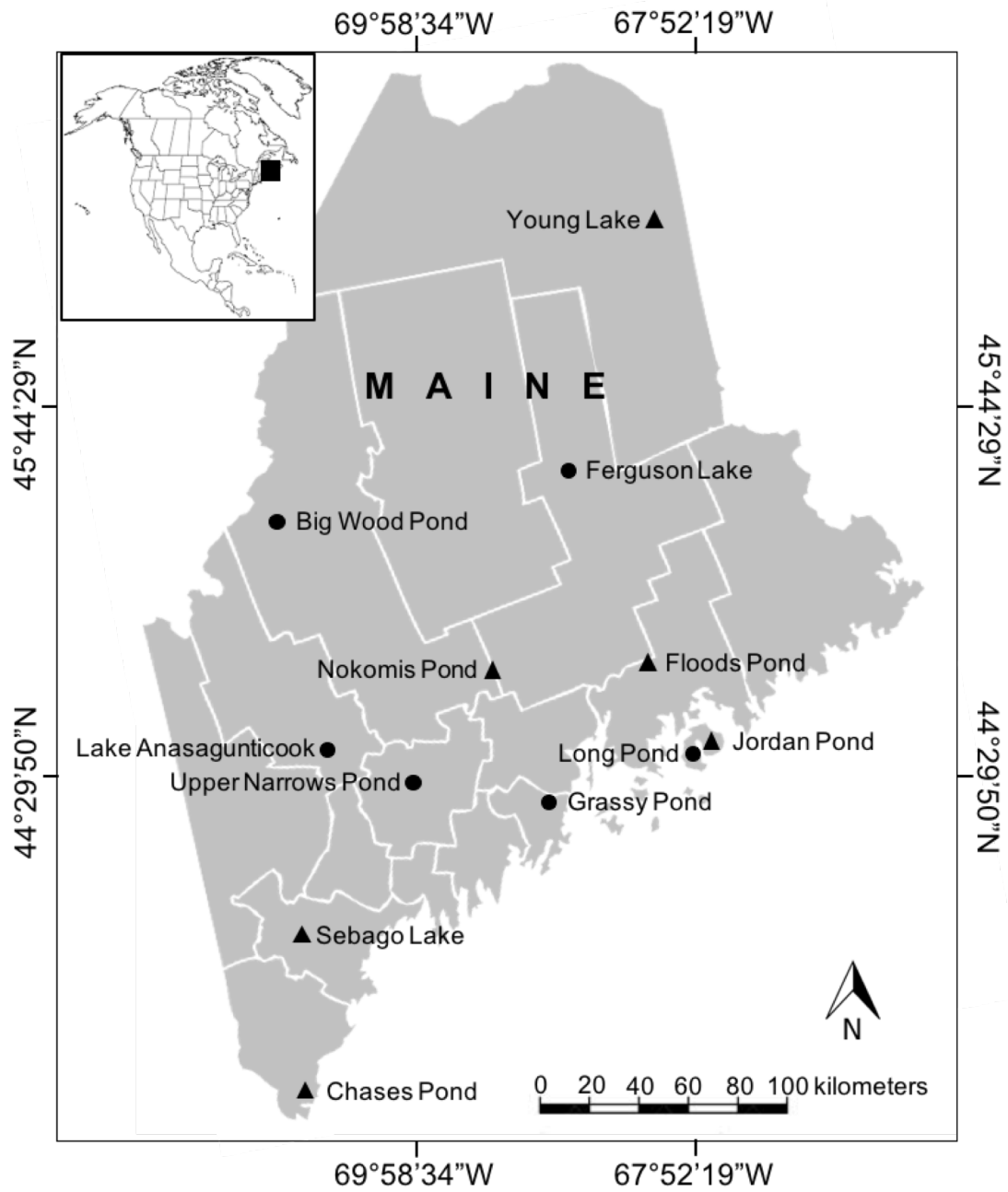


Figure 3.1. Map of the selected 12 lakes. Lakes indicated by a triangle were lakes selected for evaluating lake pre- and post-storm response.

Table 3.1. Characteristics of the 12 selected drinking water lakes across the state of Maine. Lakes indicated by a triangle were lakes selected for evaluating lake pre- and post-storm response.

Drinking Water Source	City Served	County Served	Population Served	Lake Area (km²)	Max Depth (m)	Volume (x10⁶ m³)	DOC (mg/L)
▲ Young Lake	Mars Hill	Aroostook	1,800	0.1	1	0.2	3.3
▲ Floods Pond	Bangor	Penobscot	26,500	2.6	45	32	3.5
▲ Nokomis Pond	Newport	Penobscot	1,590	0.8	7	2.2	4.6
▲ Chases Pond	York	York	11,715	0.5	11	1.7	2.7
▲ Jordan Pond	Mount Desert	Hancock	818	0.8	45	17	1.7
▲ Sebago Lake	Portland	Cumberland	136,945	121.4	96	3977	2.5
● Big Wood Pond	Jackman	Somerset	1,060	8.8	22	68	6.7
● Grassy Pond	Camden	Knox	18,185	0.8	4	0.8	3.2
● Upper Narrows Pond	Winthrop	Kennebec	2,700	1.0	16	6.1	3.5
● Ferguson Lake	Millinocket	Penobscot	5,400	1.0	8	3.0	5.6
● Lake Anasagunticook	Canton	Oxford	285	2.4	17	20	3.6
● Long Pond	Southwest Harbor	Hancock	2,380	3.8	34	33	2.8

3.3.2. Baseline sample collection

An ecological survey of the selected 12 lakes was conducted in May and August of 2014 and 2015 to provide baseline information. Temperature, Secchi depth, and pH were measured at each lake as these metrics have important relationships with DOC and water treatment. Temperature and pH values were from the upper layer of water closer to the surface, the epilimnion in each lake, which will be referred to as surface temperature. Secchi depth was used as a measure of water clarity. It was measured on the shady side of the boat using a 20 cm diameter black and white disc with an underwater viewing scope. Water was collected from the epilimnion for analysis of DOC and SUVA₂₅₄. All samples were analyzed for DOC concentration and quality immediately. DOC samples were filtered through Whatman GF/F filters pre-rinsed with deionized water. DOC concentration was analyzed on a Shimadzu Total Organic Carbon Analyzer (Shimadzu Corporation, Kyoto, Japan). A Varian Cary UV-VIS spectrophotometer was used to measure the absorbance properties within 200-800 nm wavelengths to assess DOC quality. Corrected absorbance values were calculated by subtracting a Milli-Q deionized water blank from the raw absorbance values. The following equation was used to calculate Napierian dissolved absorption coefficients (Helms et al. 2008; Kirk 2011):

$$a_d = \frac{2.303 \times D}{r}$$

where D is the decadal optical density value from the spectrophotometer and r (measured in meters) is the path length of the quartz cuvette. SUVA₂₅₄ was calculated by dividing a_d by the DOC concentration (mg L⁻¹).

3.3.3. Storm sample collection

For this study, we used samples that were collected at each of the six study lakes 24 hours before and 5-7 days after the precipitation events. The corresponding water

district collected samples for each of the six lakes from the intake inside the pump house or water treatment plant for each sampling period. Only raw (i.e., not treated) water samples were collected for analysis. One opaque 1-L pre-rinsed acid washed bottle for analysis of DOC and SUVA₂₅₄ was filled during each of the sampling periods at each lake. Each 1-L bottle was rinsed three times with lake intake water, then filled, capped, and stored in a cool dark place until shipping. After collection of the samples, bottles were shipped overnight to the University of Maine for analysis. Each sample was filtered and analyzed upon receipt as described for the baseline sample collection.

Relative Response (RR) of DOC concentrations and SUVA₂₅₄ was calculated. Post storm samples were each normalized to the pre-storm sample: $RR = (Post / Pre) - 1$. RR values less than zero indicate a decrease in that parameter, positive values indicate an increase, and zero indicates no change.

3.3.4. Watershed information

Guided by research, we evaluated landscape parameters that are strongly correlated with changes in DOC in lakes and streams include the ratio of the watershed area to lake area (WA:LA) (Schindler 1971; Engstrom 1987; Rasmussen et al 1989; Houle et al. 1995), residence time (Meili 1992), slope (Rochelle et al. 1989), and percentage of the landscape covered by wetlands (Kortelainen 1993; Watras et al. 1995; Dillon and Molot 1997). Large WA:LA ratios may be an indicator of hydrological connectivity; therefore, inputs, which may include DOC vary in lakes with different WA:LA ratios (Gergel et al. 1999). Residence time is a calculated quantity that expresses the mean amount of time that water spends in a lake. Lakes with longer residence times tend to have lower DOC concentrations than lakes with shorter residence times (Pace and Cole 2002). Slope can be related to DOC inputs, for example, lower DOC concentrations

generally correspond to higher watershed slope due to increased flow rates and reduced soil leaching time (Shang et al. 2018). The proportion of wetlands in the watershed may explain variability in DOC concentrations among lakes (Gergel et al. 1999).

Elevation data were measured using the National Elevation Dataset from the United States Geological Survey (Table 3.2). The United States Geological Survey 2011 dataset was used to measure national land cover data (NLCD). We collected information to calculate WA:LA, residence time, slope, percent coverage of wetlands, agriculture, and impervious cover within the watershed of each lake (Table 3.2). Slope was calculated using digital elevation models collected from the Maine Office of GIS. Percent wetland coverage in the watershed was calculated using the United States Fish and Wildlife Service Wetlands Mapper (www.fws.gov/wetlands/data.mapper.html; Table 3.2). Residence time was calculated as the inverse of the flushing rate, which was measured as times per year (Table 3.2).

Table 3.2. Lake and landscape variables for each of the 12 study lakes. WA:LA is the ratio of watershed area to lake area and percentages indicate the percent cover found in the watershed.

Drinking Water Source	WA:LA	Residence Time (years)	Slope (degrees)	% Land cover		
				Wetland	Agricultural	Impervious Cover
Young Lake	15.0	0.2	35.2	80	0	0.0
Floods Pond	4.3	2.6	13.7	2	0	0.2
Nokomis Pond	3.9	1.2	23.7	25	8	1.9
Chases Pond	20.0	0.3	7.8	17	1	1.0
Sebago Lake	3.8	6.7	6.7	8	1	1.0
Jordan Pond	5.0	5.9	47.5	3	0	1.4
Big Wood Pond	8.0	0.2	16.8	8	0	0.5
Grassy Pond	6.5	0.2	13.4	20	4	1.8
Upper Narrows Pond	10.3	0.7	7.3	6	3	2.1
Ferguson Lake	1.9	2.5	25.6	4	0	1.0
Lake Anasagunticook	14.5	0.9	22.8	15	5	1.4
Long Pond	3.4	3.1	27.7	9	0	0.5

3.3.5. Estimating welfare impacts of changing water quality

Valuing water quality is challenging because there is not a singular method to quantify all of the measurable attributes of water (e.g. recreational use, property value, consumption, etc.) (Keeler et al. 2012). There are several methods (e.g., hedonic, travel cost, stated preference) that have been used, including benefit transfer. The process of benefit transfer involves transferring information from one site to another (Downing and Ozuna 1996; Rosenberger and Loomis 2003). This approach can yield statistically similar estimates between the referred site and the policy site, however when non-linear models are used to estimate benefit functions, the reliability of the transfer may be reduced (Downing and Ozuna 1996; Rosenberger and Loomis 2003).

In this study we chose to apply a previously completed meta-analysis as it was the most directly related to our study. Data were not available to calculate total costs of drinking water treatment from the drinking water utilities. Cost estimates for treatment vary significantly between water utilities and are dependent on the methods used. Additionally, water treatment managers are hesitant to distribute information due to potentially large costs associated with altering or implementing new treatment strategies. Therefore, we estimated welfare impacts using a benefit function transfer associated with a published meta-analysis (Ge et al. 2013). The purpose of the meta-analysis was to construct a valuation function from estimates in existing studies or a benefit transfer. This valuation function can then be used to calculate benefit and cost estimates in different settings (Ge et al. 2013). We used a meta-analysis from Ge et al. (2013) to calculate estimated losses from changes in water quality in the selected lakes, attempting to transfer the entire benefit function, described below.

This meta-analysis measured water quality changes using changes in Secchi depth. Ge et al. (2013) used a scientific data mining software to identify a function to explain the relationship between an established indicator of water quality change, known as a water quality index (WQI), and Secchi depth. Secchi depth is a common measurement collected in many lakes, and the reason for establishing a relationship with the WQI is to enable researchers to universally apply the meta-analysis to other studies. The function selected to convert the WQI to Secchi depth is:

$$WQI = 78.9 + S + \frac{1.95}{0.06 - S^2}$$

where S is Secchi depth. WQI and Secchi depth have a positive relationship. When Secchi values are small, or the water is less clear, a small increase in Secchi depth results in a relatively large increase in the WQI. As Secchi depth becomes deeper, or the lakes are clearer, the curve becomes flatter and an increase in Secchi depth will not lead to as large of an increase in the WQI (Figure 3.2; Ge et al. 2013). This function allowed us to use measures of Secchi depth to evaluate losses due to changes in water quality from storm events.

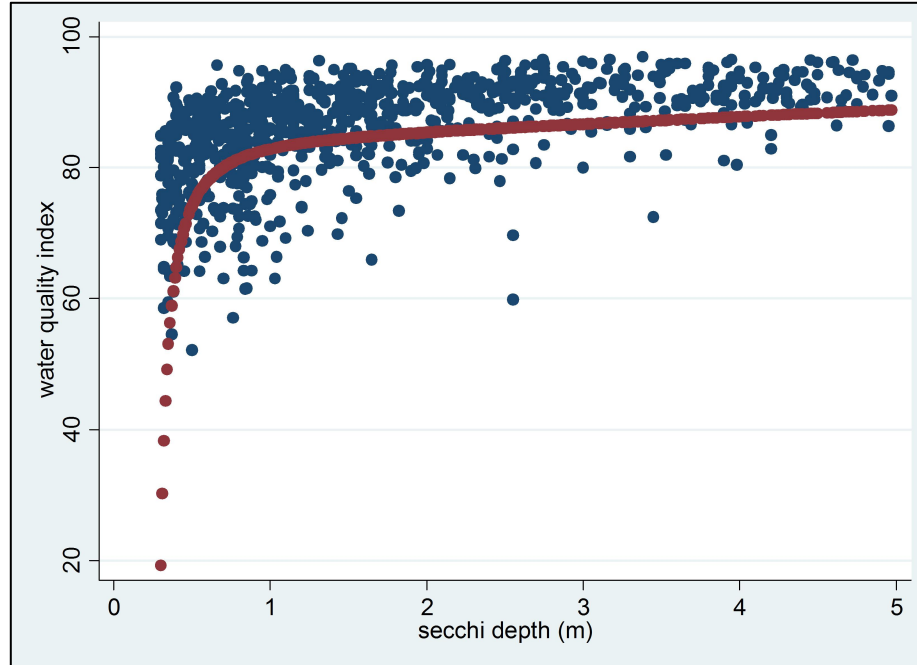


Figure 3.2. Relationship between Secchi depth and water quality index. Figure from Ge et al. 2013.

In Ge et al. (2013), WTP for changes in water quality was defined as a function dependent on the initial water quality (WQI^0), the change in water quality (ΔWQI), and other control variables (Ge et al. 2013). Our calculation does not include all of the control variables from Ge et al (2013) but takes the estimated parameters from their work and pairs them with the variables represented by the data we have available. This is represented by the following:

$$WTP = 27.94(Northeast) + 287.23(Lake) - 2.67(WQI^0 + 4.48(\Delta WQI) + 0.06(Lake\ Size) - 0.004(Region\ Size)$$

Ge et al. (2013) used a linear regression model to estimate this WTP function. This function was then applied to Maine drinking water lakes to estimate welfare changes based on changing Secchi depth from changes in precipitation and subsequent changes in DOC. The dependent variable is WTP per household in 2010 U.S. dollars, which were converted to 2018 U.S. dollars using the Consumer Price Index provided by the U.S.

Department of Labor and Bureau of Labor Statistics (<https://www.usinflationcalculator.com/inflation/consumer-price-index-and-annual-percent-changes-from-1913-to-2008>). The independent variables include the initial or starting WQI and the change in the WQI. The control variables include region (in this study, the northeastern U.S.), the water body type (in this study, a lake), the size of the lake, and region size; we used a 5-mile radius as it was closest to the actual population served by the drinking water resource listed by the Maine Center for Disease Control (<https://www.maine.gov/dhhs/mecdc/environmental-health/dwp/sitemap/surfaceWater.shtml>).

For the purposes of this study, precipitation events contribute to a reduction in water quality, rather than an improvement in water clarity; therefore, WTP would typically not be an appropriate measure to quantify estimates from a storm event. A consumer of the drinking water resource would be willing to accept a payment to agree to the reduction in water quality due to a storm event. WTP reflects the maximum amount an individual would pay to obtain a good, while willingness to accept (WTA) reflects a minimum payment amount to relinquish a good (Brown and Gregory 1999). Typically, WTP estimates are associated with an improvement or gain, while WTA would be appropriate for resource damages (Bromley, 1995). The caveat to using WTA versus WTP is that WTA is commonly undervalued when measuring environmental goods (Brown and Gregory 1999; Huang et al. 2013; Booth et al. 2016). Ge et al. (2013) evaluate WTP for an improvement in water quality; this function is applied to this study to provide estimated losses based on reductions in water quality due to changes in Secchi depth. Since WTP is expected to be less than WTA, the WTP results of this study will provide a conservative lower bound of the true WTA measure.

This calculation was used in the 12 study lakes. Relationships between DOC and Secchi were explored to try and establish a link between the ecological change and economic meta-analysis. The resulting losses from a reduction in water quality were explored for 1 m, 2 m, and 4 m changes in Secchi depth. A discount rate of 2.75%, set by the United States Department of Agriculture and the Natural Resources Conservation Service, was used to calculate the net present value of the estimated losses. This discount rate represents the discount rate for the fiscal year 2018 Water Resources Planning and Evaluation (https://www.nrcs.usda.gov/wps/portal/nrcs/detail/national/cntsc/?cid=nrcs143_00). Net present value was used to calculate the current monetary value of the future losses and it is the sum of the discounted estimated losses for each year, represented by the following:

$$Net\ Present\ Value = \sum \frac{Year\ n\ Losses}{(1 + Discount\ Rate)^n}$$

where n represents year. Net present value for the annual losses per household was calculated for the current year and also for a 30-year timeframe to identify longer term losses. Aggregate losses for all households within the 5-mile radius was calculated by multiplying the annual losses per household by the population for each the current year and the 30-year timeframe.

3.3.6. Data analysis

To assess differences in initial physical (Secchi depth, temperature) and chemical (pH, DOC, SUVA₂₅₄) parameters for the 12 lakes included in the baseline sampling, a one-way analysis of variance (ANOVA) was used to compare the means of the parameters. The ANOVA allowed us to identify initial differences among the lakes selected for this study. Levene's test for homogeneity and Shapiro-Wilks normality test were used to test for the assumptions of ANOVA. A significance level of $p < 0.05$ was

used and Tukey's honestly significant differences post-hoc test was used to determine which means were significantly different from one another. For the same set of lakes, simple linear regression was used to assess relationships between lake and watershed characteristics, including maximum depth, WA:LA, residence time, total percent wetland coverage, Secchi depth, and DOC concentration and SUVA₂₅₄. DOC and SUVA₂₅₄ values were log transformed to meet assumptions of normality and constant variance and linear relationships were considered significant if $p < 0.05$.

Simple linear regression was used to assess if maximum depth, WA:LA, residence time, or total percent wetland coverage affected the mean percent change in DOC concentration and SUVA₂₅₄ to storms for each of the six in-depth study lakes. Mean percent change is the average percent change between pre- and post-storm samples (collected 5-7 days after the precipitation event). Linear regression was also used to assess the relationship between precipitation amounts at each lake for each storm and the percent change in DOC concentration and percent change in SUVA₂₅₄. Relationships were considered significant if $p < 0.05$.

Relationships between mean Secchi depth (from the baseline sampling) and the mean percent change in DOC concentration and SUVA₂₅₄ were explored to identify the relationship between Secchi depth and changes in DOC and SUVA₂₅₄ from a storm event for the six in-depth study lakes. A significance level of $p < 0.05$ was used. This function was used to estimate percent change in DOC concentration and SUVA₂₅₄ for an average storm event based on a lake's initial Secchi depth.

Pearson's correlation coefficient was used to evaluate correlations between lake and watershed attributes and population size and estimated losses from reductions in

water clarity for the current year and for a 30-year timeframe for the 12 lakes.

Correlations were considered significant if $p < 0.10$.

ANOVA was used to compare welfare estimates between lakes with Secchi depths from 2 to 4 meters, 4 to 6 meters and greater than 6 meters. The ANOVA allowed us to compare the welfare estimates for lakes with different initial water quality. ANOVA was also used to compare aggregate welfare estimates between drinking water lakes. Levene's test for homogeneity and Shapiro-Wilks normality test were used to test for the assumptions of ANOVA. Annual estimates were calculated assuming a constant number of days of losses per year, therefore the losses were not related to predicted increases in frequency of precipitation events. A significance level of $p < 0.05$ was used and Tukey's honestly significant differences post-hoc test was used to determine which means were significantly different from one another. All statistical analyses were conducted using R software (version 3.2.1, The R Foundation for Statistical Computing, 2015).

3.4 Results

3.4.1. Baseline sample collection

Physical parameters including Secchi depth and surface temperature varied across lakes with significant differences between Secchi readings in some lakes and no significant differences detected in temperature among all lakes (Table 3.3). Mean Secchi depth measurements ranged from 2.4 m in Young Lake to 11.5 m in Jordan Pond (Table 3.3). Sebago Lake, Jordan Pond, and Long Pond had deeper Secchi depths than the remaining nine lakes ($p < 0.05$). Young Lake, Big Wood Pond, and Grassy Pond had shallower Secchi depths compared to the remaining eight lakes ($p < 0.05$). Mean surface temperature ranged from 17.4°C to 21.9°C (Table 3.3).

Chemical characteristics including pH, DOC concentration, and SUVA₂₅₄ varied among the lakes. DOC concentration ranged from 1.8 mg L⁻¹ in Jordan Pond to 6.8 mg L⁻¹ in Big Wood Pond (Table 3.3). DOC concentration in Big Wood Pond was higher than the eleven remaining lakes and DOC concentration in Jordan Pond was lower than all of the remaining lakes except Sebago Lake ($p < 0.05$). Ferguson Lake and Nokomis Pond DOC concentrations were higher than all of the other lakes except Big Wood Pond ($p < 0.05$). SUVA₂₅₄ ranged from 5.2 L mg-C⁻¹ m⁻¹ in Jordan Pond to 9.8 L mg-C⁻¹ m⁻¹ in Big Wood Pond (Table 3.3). SUVA₂₅₄ was lower in Jordan Pond compared to Nokomis Pond, Grassy Pond, Ferguson Lake, and Big Wood Pond ($p < 0.05$), higher in Ferguson Lake and Big Wood Pond than in Sebago Lake and Chases Pond ($p < 0.05$), and higher in Big Wood Pond than Upper Narrows Pond and Long Pond ($p < 0.05$). The pH levels ranged from 6.4 in Chases Pond to 7.6 in Young Lake (Table 3.3). Young Lake had higher pH than Long Pond, Jordan Pond, and Grassy Pond ($p < 0.05$), the pH in Upper Narrows Pond was higher than Grassy Pond ($p < 0.05$), and Chases Pond had lower pH than Young Lake, Upper Narrows Pond, Nokomis Pond, and Lake Anasagunticook ($p < 0.05$).

Table 3.3. Select characteristics of the study lakes from baseline sample collection. Numbers are average measurements (\pm standard error) of baseline data collected in May and August of 2014 and 2015.

Drinking Water Source	Secchi Depth (m)	Surface Temperature ($^{\circ}$ C)	pH	DOC (mg L ⁻¹)	SUVA ₂₅₄ (L mg-C ⁻¹ m ⁻¹)
Young Lake	2.4 \pm 0.0	18.0 \pm 1.8	7.6 \pm 0.0	3.6 \pm 0.6	7.6 \pm 0.4
Floods Pond	6.7 \pm 0.3	20.2 \pm 1.9	6.8 \pm 0.0	3.6 \pm 0.1	7.3 \pm 0.4
Nokomis Pond	5.1 \pm 0.8	21.0 \pm 2.0	7.4 \pm 0.0	4.7 \pm 0.1	8.1 \pm 0.8
Chases Pond	5.1 \pm 0.2	21.9 \pm 1.2	6.4 \pm 0.2	2.9 \pm 0.1	6.2 \pm 0.7
Jordan Pond	11.5 \pm 0.7	17.9 \pm 3.0	6.8 \pm 0.0	1.8 \pm 0.1	5.2 \pm 0.0
Sebago Lake	9.8 \pm 0.4	18.7 \pm 2.7	7.2 \pm 0.1	2.6 \pm 0.0	6.2 \pm 0.2
Big Wood Pond	3.4 \pm 0.2	17.4 \pm 2.7	7.0 \pm 0.2	6.8 \pm 0.2	9.8 \pm 0.5
Grassy Pond	3.9 \pm 0.3	21.7 \pm 1.8	6.6 \pm 0.4	3.1 \pm 0.3	7.8 \pm 0.1
Upper Narrows Pond	4.5 \pm 0.5	21.0 \pm 2.0	7.4 \pm 0.1	3.7 \pm 0.2	6.9 \pm 0.5
Ferguson Lake	4.4 \pm 0.4	19.1 \pm 2.1	7.1 \pm 0.1	5.7 \pm 0.1	9.0 \pm 0.5
Lake Anasagunticook	5.0 \pm 0.3	20.3 \pm 3.5	7.3 \pm 0.0	3.6 \pm 0.1	7.3 \pm 0.3
Long Pond	8.2 \pm 0.4	18.7 \pm 2.8	6.7 \pm 0.1	3.0 \pm 0.1	6.5 \pm 0.2

Secchi depth was negatively correlated with DOC and SUVA₂₅₄ ($p < 0.05$; Figure 3.3). Maximum depth, WA:LA, and residence time were negatively correlated with DOC and SUVA₂₅₄, however they were not significant (Figure 3.3). There was no significant relationship between percent wetland coverage in the watershed and initial concentrations of DOC or SUVA₂₅₄ (Figure 3.3).

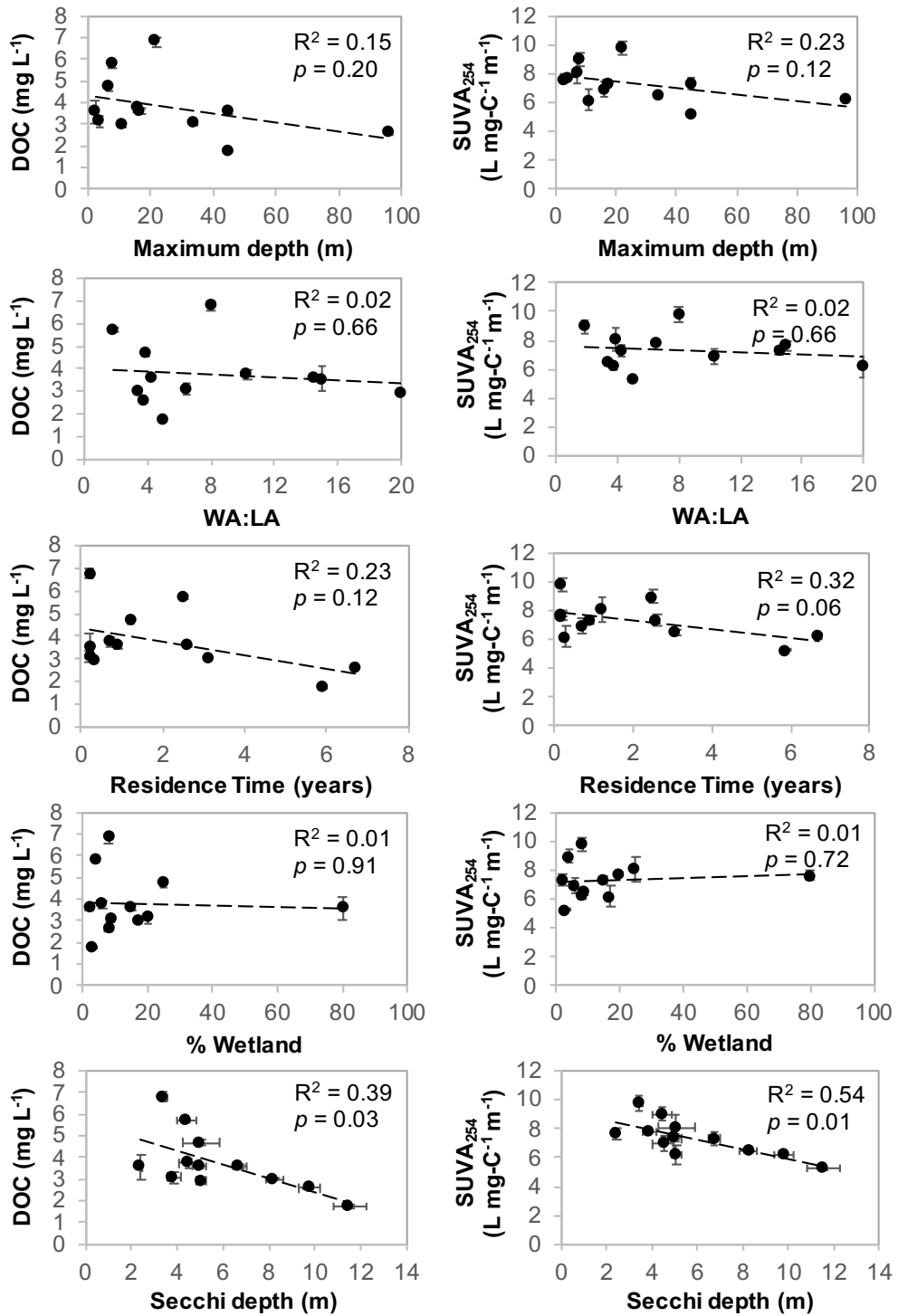


Figure 3.3. Relationships between DOC or SUVA₂₅₄ and lake and landscape variables for the 12 initial study lakes. Lake and landscape variables include maximum depth, WA:LA (Watershed Area:Lake Area), residence time (measured in years), percent wetland in the watershed, or Secchi depth.

3.4.2. Storm sample collection

Opposite of the relationship with initial DOC concentrations, percent wetland coverage in the watershed had a positive effect on the mean percent change in DOC and the mean percent change in SUVA₂₅₄ from a storm event ($p < 0.05$; Figure 3.4); however, this relationship is driven by Young Lake. Maximum depth and residence time were negatively correlated with mean percent change in DOC and mean percent change in SUVA₂₅₄, however they were not significant (Figure 3.4). There were no significant relationships between mean percent change in DOC or mean percent change in SUVA₂₅₄ with respect to WA:LA (Figure 3.4).

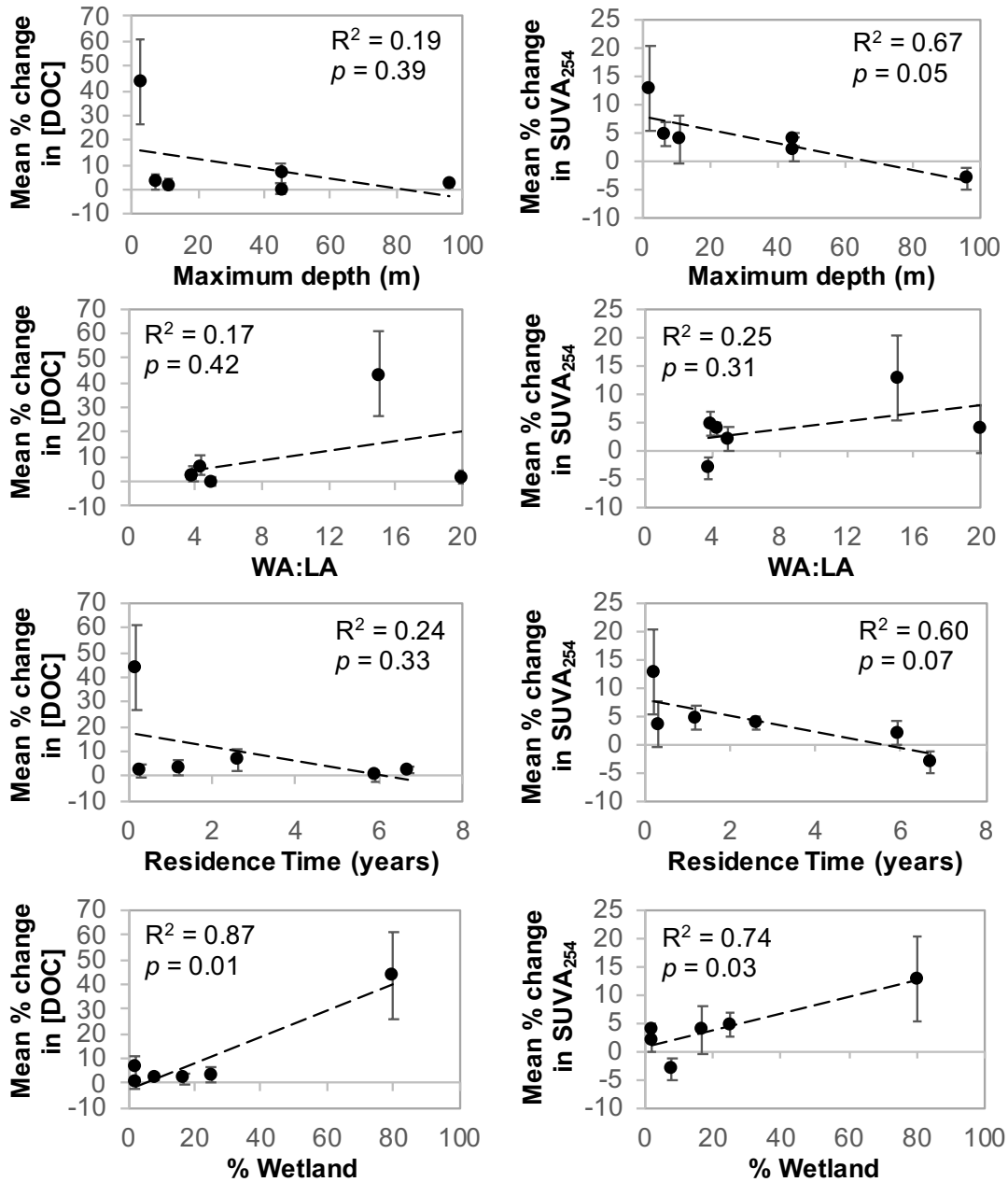


Figure 3.4. Relationships between mean percent change in DOC or SUVA₂₅₄ (\pm standard error) and lake and landscape variables for the 6 in-depth study lakes. Lake and landscape variables include maximum depth, WA:LA (Watershed Area:Lake Area), residence time (measured in years), or percent wetland in the watershed. Values for each lake are averaged across the 5 storms. Percent change was calculated from pre-storm to post storm collection, 5-7 days after the storm events. Bars indicate standard error.

In general, precipitation was positively correlated with percent change in DOC and with percent change in SUVA₂₅₄ with the exception of the relationship between precipitation and SUVA₂₅₄ in Jordan Pond and Sebago Lake, which was negative (Figure 3.5). Mean percent change in DOC concentration in Floods Pond, Jordan Pond, and Sebago Lake were correlated with precipitation amount ($p < 0.05$; Figure 3.5), and mean percent change in SUVA₂₅₄ in Floods Pond and Nokomis Pond were correlated with precipitation amount ($p < 0.05$; Figure 3.5).

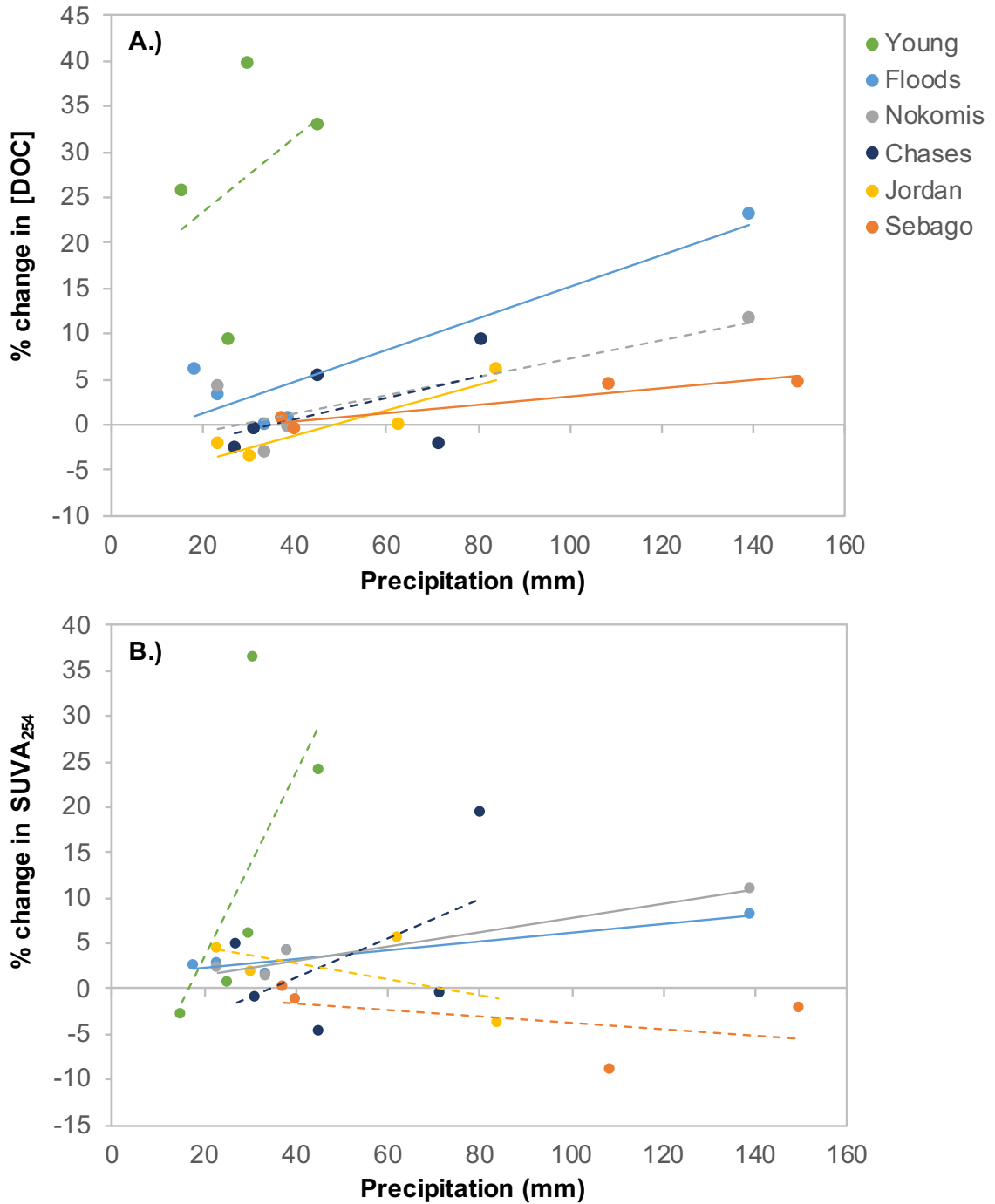


Figure 3.5. Relationships between storm precipitation amounts and A.) percent change in DOC or B.) percent change in SUVA₂₅₄ for the 6 in-depth study lakes. Percent change in DOC and SUVA₂₅₄ represent the change for that corresponding storm from pre- to post-storm, 5-7 days after the storm events. Significant trends are indicated by solid lines ($p < 0.05$).

Mean Secchi depth and the mean percent change in DOC concentrations as well as mean percent change in SUVA₂₅₄ were related to estimate the relationship between DOC or SUVA₂₅₄ and Secchi depth (Figure 3.6). The relationships between mean Secchi depth and mean percent change in DOC and mean percent change in SUVA₂₅₄ are significant ($p < 0.05$; Figure 3.6). Lakes with Secchi depths deeper than 4 m have smaller mean percent change in DOC concentrations from storm events and are less variable than lakes with Secchi depths shallower than 4 m ($p < 0.05$; Figure 3.6). Lakes with Secchi depths between 2 and 6 m have more variable mean percent change in SUVA₂₅₄ than lakes with Secchi depth measurements deeper than 6 m ($p < 0.05$; Figure 3.6).

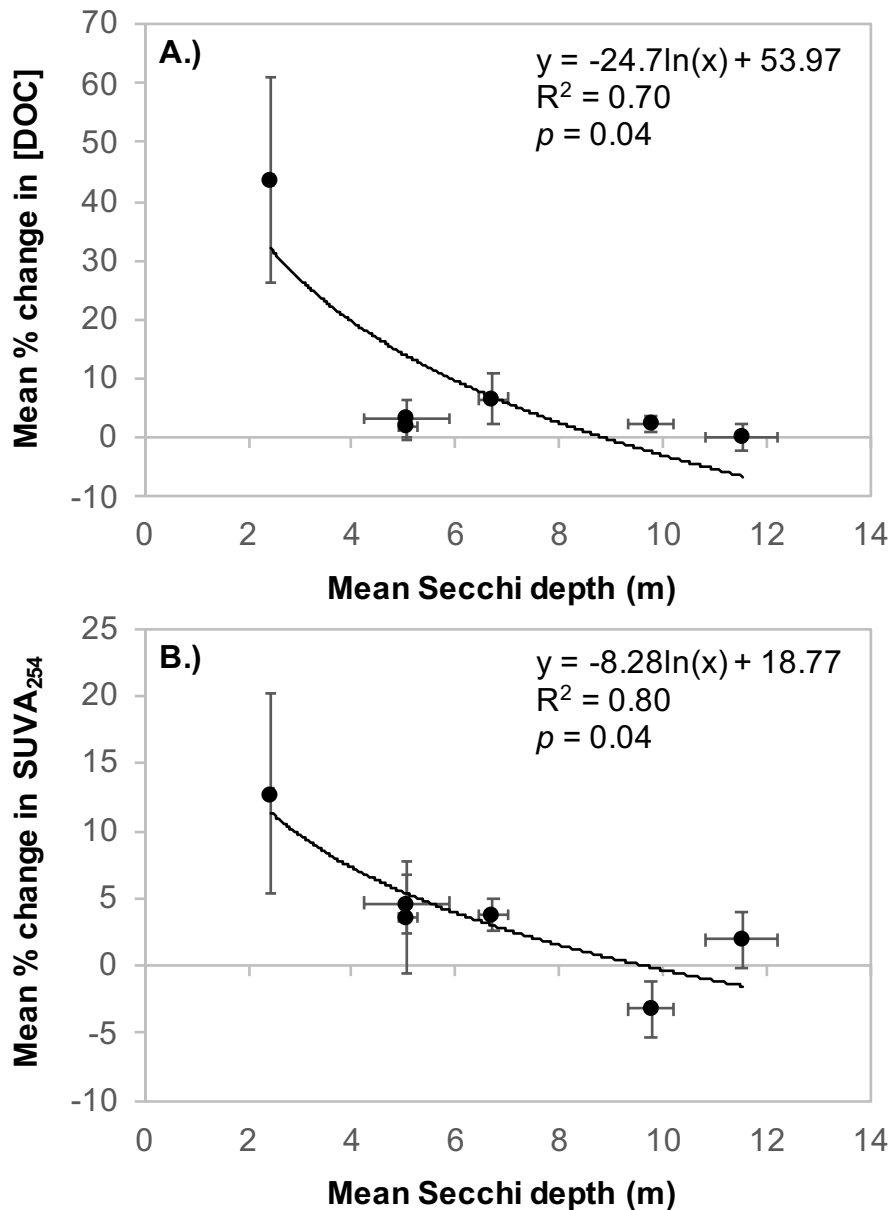


Figure 3.6. Relationship between mean Secchi depth and A.) percent change in DOC or B.) percent change SUVA₂₅₄ for the 6 in-depth study lakes. Secchi depth measurements are from baseline sampling in May and August 2014 and 2015. A logarithmic trendline is fit to the data with the associated R² values. Solid lines indicate significant trends ($p < 0.05$).

The equation generated by the relationship between Secchi depth and percent change in DOC and percent change in SUVA₂₅₄ was used to estimate the potential change in DOC from a rain event. Lakes with shallower Secchi depths correspond to a larger percent change in DOC and a larger percent change in SUVA₂₅₄ (Table 3.4).

Table 3.4. Expected mean percent change in DOC and SUVA₂₅₄ based on average Secchi depth from a storm event with between 25.4 and 80 mm of rainfall.

Drinking Water Source	% change in [DOC]	% change in SUVA₂₅₄	Mean Secchi depth (m)
Young Lake	+31.9	+11.4	2.4±0.0
Floods Pond	+6.9	+3.0	6.7±0.3
Nokomis Pond	+14.0	+5.4	5.1±0.8
Chases Pond	+13.9	+5.3	5.1±0.2
Jordan Pond	-6.4	-1.5	11.5±0.7
Sebago Lake	-2.3	-0.1	9.8±0.4
Big Wood Pond	+23.6	+8.6	3.4±0.2
Grassy Pond	+20.6	+7.6	3.9±0.3
Upper Narrows Pond	+16.8	+6.3	4.5±0.5
Ferguson Lake	+17.3	+6.5	4.4±0.4
Lake Anasagunticook	+14.3	+5.5	5.0±0.3
Long Pond	+1.9	+1.3	8.2±0.4

3.4.3. Estimating welfare impacts of changing water quality

Annual losses per household within a 5 square mile radius of each lakes for changes in water quality was largest in lakes with higher DOC concentrations, higher SUVA₂₅₄, and shallower initial Secchi depths. For both the current year and 30-year timeframes for a 1m decline in Secchi depth, lakes with Secchi depths that ranged from 2 to 4 m had higher losses than lakes with Secchi depths deeper than 6 m ($p < 0.01$; Table 3.5), and lakes with Secchi depths that ranged from 4 to 6 m had higher losses than lakes with Secchi depths deeper than 6 m ($p < 0.01$; Table 3.5). For a 2m decline in Secchi depth for both the current year and 30-year timeframes lakes with Secchi depths that ranged from 2 to 4 m had higher losses than lakes with Secchi depths deeper than 6 m (p

< 0.02; Table 3.5). For both the current year and 30-year timeframes for a 4 m decline in Secchi depth lakes with Secchi depths that ranged from 2 to 4 m had higher losses than lakes with Secchi depths that ranged from 4 to 6 m as well as Secchi depths deeper than 6 m ($p < 0.01$; Table 3.5).

Table 3.5. Estimated losses from reductions in water quality for the current year and for a 30-year timeframe. Losses are calculated with a 2.75% discount rate per household within a 5 square mile region for each lake. Water quality reduction is designated by a decrease in Secchi depth (decreased water clarity) Values in 2018 U.S. dollars. Secchi depth measured in meters.

Drinking Water Source	Secchi depth range (m)	Current year				30-year timeframe			
		1 meter	2 meters	4 meters	1 meter	1 meter	2 meters	4 meters	
Young Lake	2-4	-121.40	-174.91	-458.33	-2,525.82	-3,639.22	-9,536.13		
Big Wood Pond	2-4	-115.91	-124.04	-460.97	-2,411.63	-2,580.74	-9,591.05		
Grassy Pond	2-4	-113.74	-120.32	-226.63	-2,366.44	-2,503.49	-4,715.23		
Ferguson Lake	4-6	-111.96	-117.92	-179.56	-2,329.44	-2,453.42	-3,735.93		
Upper Narrows Pond	4-6	-110.27	-115.92	-135.81	-2,294.21	-2,411.83	-2,825.77		
Lake Anasagunticook	4-6	-110.30	-115.96	-135.85	-2,294.99	-2,412.61	-2,826.55		
Nokomis Pond	4-6	-111.95	-117.91	-179.55	-2,329.33	-2,453.31	-3,735.82		
Chases Pond	4-6	-110.25	-115.91	-135.80	-2,294.93	-2,411.55	-2,825.49		
Floods Pond	4-6	-105.47	-110.79	-122.23	-2,194.33	-2,305.10	-2,543.23		
Long Pond	> 6	-100.79	-106.02	-116.69	-2,097.06	-2,205.95	-2,427.93		
Sebago Lake	> 6	-97.71	-102.91	-113.34	-2,032.95	-2,140.98	-2,358.21		
Jordan Pond	> 6	-88.32	-93.50	-103.88	-1,837.69	-1,945.40	-2,161.25		

Correlations between lake and watershed variables and losses suggest maximum depth, residence time, percent wetland, SUVA₂₅₄, and DOC concentration are important for determining losses. Maximum depth was negatively correlated with losses for a 1 m decline in Secchi depth for the current year ($r = -0.73$; $p < 0.01$) and for a 30-year timeframe ($r = -0.73$; $p < 0.01$; Figure 3.7; Table 3.6). Maximum depth was negatively correlated with losses for a 2 m decline in Secchi depth for the current year ($r = -0.53$; $p < 0.05$) and for a 30-year timeframe ($r = -0.53$; $p < 0.05$; Figure 3.7; Table 3.6). There was a negative correlation between residence time and losses for the current year for a 1 m ($r = -0.88$; $p < 0.01$), 2 m ($r = -0.60$; $p < 0.05$), and 4 m ($r = -0.52$; $p < 0.10$) decline in Secchi depth, and for a 30-year timeframe for 1 m ($r = -0.88$; $p < 0.01$), 2 m ($r = -0.60$; $p < 0.05$), and 4 m ($r = -0.52$; $p < 0.10$) reductions in Secchi depth (Figure 3.7; Table 3.6). The percent wetland coverage in the watershed was positively correlated with losses for the current year for 1 m ($r = 0.58$; $p < 0.05$), 2 m ($r = 0.92$; $p < 0.01$), and 4 m ($r = 0.63$; $p < 0.10$) reductions in Secchi depth, and for a 30-year timeframe for 1 m ($r = 0.58$; $p < 0.05$), 2 m ($r = 0.92$; $p < 0.01$), and 4 m ($r = 0.63$; $p < 0.10$) reductions in Secchi depth (Figure 3.7; Table 3.6). SUVA₂₅₄ was positively correlated with losses for a 1 m decline in Secchi depth for the current year ($r = 0.74$; $p < 0.01$) and for a 30-year timeframe ($r = 0.74$; $p < 0.01$) and positively correlated with losses for a 4 m decline in Secchi depth for the current year ($r = 0.65$; $p < 0.05$) and for a 30-year timeframe ($r = 0.65$; $p < 0.05$; Figure 3.7; Table 3.6). DOC concentration was also positively correlated with losses for a 1 m decline in Secchi depth for the current year ($r = 0.62$; $p < 0.05$) and for a 30-year timeframe ($r = 0.62$; $p < 0.05$) and positively correlated with losses for a 4 m decline in Secchi depth for the current year ($r = 0.57$; $p < 0.10$) and for a 30-year timeframe ($r = 0.57$; $p < 0.10$; Figure 3.7; Table 3.6).

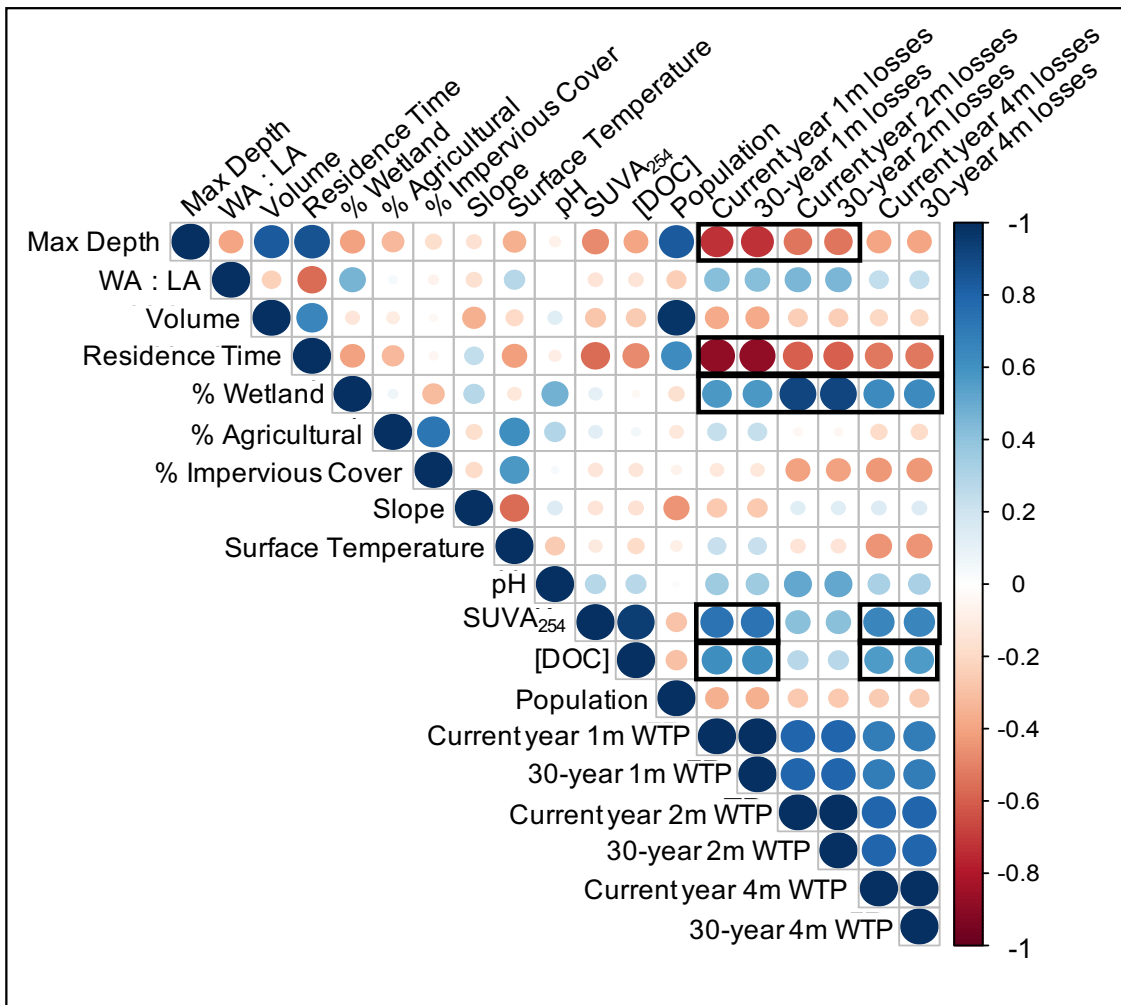


Figure 3.7. Correlations between lake or watershed variables and estimated losses from reductions in water clarity. Estimated losses are for the current year and over a 30-year timeframe for 1m, 2m, and 4m changes in water clarity. Circles within black boxes indicate significant relationships ($p < 0.05$) between lake or watershed variables and willingness to pay. WA:LA indicates the ratio of watershed area to lake area. Correlations are based on data per household.

Table 3.6. Correlation (r) values between key lake features and estimated losses from reductions in water clarity. Estimated losses are for the current year and over a 30-year timeframe for 1m, 2m, and 4m changes in water quality.

Lake Variable	Current year			30-year timeframe		
	<i>1 meter</i>	<i>2 meters</i>	<i>4 meters</i>	<i>1 meter</i>	<i>2 meters</i>	<i>4 meters</i>
Max Depth	-0.73 ^{***}	-0.53 ^{**}	-0.40	-0.73 ^{***}	-0.53 ^{**}	-0.40
Residence Time	-0.88 ^{***}	-0.60 ^{**}	-0.52 [*]	-0.88 ^{***}	-0.60 ^{**}	-0.52 [*]
% Wetland	0.58 ^{**}	0.92 ^{***}	0.63 [*]	0.58 ^{**}	0.92 ^{***}	0.63 [*]
Secchi Depth	-0.99 ^{***}	-0.74 ^{**}	-0.65 [*]	-0.99 ^{***}	-0.74 ^{**}	-0.65 [*]
SUVA ₂₅₄	0.74 ^{***}	0.42	0.65 ^{**}	0.74 ^{***}	0.42	0.65 ^{**}
[DOC]	0.62 ^{**}	0.28	0.57 [*]	0.62 ^{**}	0.28	0.57 [*]

*** $p < 0.01$; ** $p < 0.05$; * $p < 0.10$

Aggregate annual losses for all households in a 5-mile radius was variable and directly correlated to the size of the population served by the drinking water resource and not correlated to initial Secchi depth. Welfare estimates for changes in water quality for the current year and 30-year timeframes were highest in Sebago lake ($p < 0.01$) and lowest in Big Wood Pond and Lake Anasagunticook ($p < 0.01$; Table 3.7).

Table 3.7. Aggregate estimated losses from reductions in water clarity for the current year and for a 30-year timeframe. Losses are calculated with a 2.75% discount rate within a 5 square mile region for each lake. Water quality reduction is designated by a decrease in Secchi depth (decreased water clarity) Values in 2018 U.S. dollars. Secchi depth measured in meters.

Drinking Water Source	Secchi depth range (m)	Current year			30-year timeframe		
		1 meter	2 meters	4 meters	1 meter	2 meters	4 meters
Young Lake	2-4	-106,392	-153,291	-401,680	-2,213,611	-3,189,397	-8,357,417
Big Wood Pond	2-4	-42,882	-45,888	-170,540	-892,201	-954,761	-3,548,278
Grassy Pond	2-4	-474,280	-501,748	-945,024	-9,867,944	-10,439,444	-19,662,322
Ferguson Lake	4-6	-216,518	-228,042	-347,250	-4,504,911	-4,744,684	-7,224,937
Upper Narrows Pond	4-6	-410,397	-431,438	-505,485	-8,538,790	-8,976,564	-10,517,200
Lake Anasagunticook	4-6	-46,867	-49,269	-57,772	-975,123	-1,025,099	-1,200,979
Nokomis Pond	4-6	-252,785	-266,240	-405,421	-5,259,478	-5,539,426	-8,435,256
Chases Pond	4-6	-976,705	-1,026,785	-1,203,032	-20,321,475	-21,321,460	-25,030,466
Floods Pond	4-6	-234,660	-246,506	-271,971	-2,095,440	-2,201,222	-2,428,618
Long Pond	> 6	-315,262	-331,631	-365,004	-6,559,385	-6,899,972	-7,594,324
Sebago Lake	> 6	-2,455,309	-2,585,779	-2,848,140	-51,085,540	-53,800,132	-59,258,849
Jordan Pond	> 6	-198,446	-210,076	-233,386	-4,128,893	-4,370,879	-4,855,866

3.5. Discussion

Our results reveal that percent change in DOC and percent change in SUVA₂₅₄ during a precipitation event correspond to initial Secchi depth values; lakes with shallower Secchi depths had a higher percent change and were more variable in response to storms than lakes with deeper Secchi depths. Losses from reduced water clarity was related to initial Secchi depths, with lakes that have shallower Secchi depths corresponding to higher losses compared to lakes with deeper Secchi depths. Additionally, losses were influenced by the maximum depth of the lake, residence time, percent of wetland coverage, DOC concentrations and SUVA₂₅₄. These findings suggest that estimated losses are likely correlated to changes in DOC from precipitation events. This information provides important insights to assist in managing drinking water resources and the implications from precipitation events.

Evaluating the relationships between DOC and lake and watershed variables is important for understanding why changes in DOC may occur due to a precipitation event. Previous work suggests that how DOC and SUVA₂₅₄ respond to precipitation events is dependent on residence time and that WA:LA could also be important in determining lake response (Warner and Saros, 2019). These same lake and landscape features are also important for determining estimated losses for reduced water quality. By evaluating the relationships between the costs generated by implementing the function from the meta-analysis by Ge et al. (2013) and the lake and watershed variables, the relationships accurately reflect parameters that, if changed, would likely impact costs.

Evaluation of relationships between lake and watershed variables and DOC concentrations and SUVA₂₅₄ were important in identifying the relationship between DOC or SUVA₂₅₄ and estimated losses. While the relationships between DOC or SUVA₂₅₄ and

Secchi depth is significant based on the initial baseline sampling, not considering other variables would not allow drinking water managers to accurately discern how storm events may impact losses. Maximum depth and residence time were not significant in the baseline sampling, but negative relationships were revealed. Further investigation of the percent change in DOC and SUVA₂₅₄ to storm events revealed significant relationships with residence time and wetlands as well as between SUVA₂₅₄ and maximum depth. Shorter residence time in lakes may result from increased precipitation events and contribute to increases in DOC (Tranvik et al. 2009). The percent wetland coverage had a significant relationship with the mean percent change in DOC and SUVA₂₅₄ but not with initial concentrations. The relationships between DOC concentration and wetlands have been previously documented (Kortelainen 1993) and suggest that the extent of wetlands is correlated to DOC export (Dillon and Molot 1997), therefore this may be exacerbated by increasing precipitation events. The correlations between lake variables and estimated losses reveal the same parameters identified as important to percent change in DOC or SUVA₂₅₄ (maximum depth, residence time, and wetlands) are modifying losses. For example, shallower lakes with short residence time and a higher percentage of wetland coverage have higher losses. Indirectly, these relationships are important in estimating losses, as they can be related to Secchi depth measurements.

The amount of precipitation during a storm event is also important for the response of DOC and SUVA₂₅₄. Research by Strock et al (2017) suggests that DOC increased in a remote set of lakes in the northeast during an extreme wet year. While this study does not allow for evaluation of specific rain amounts from a particular storm on lakes due to the spatial variation of lakes across Maine as well as differences in climate, the relationship between precipitation and change in DOC and SUVA₂₅₄ suggests that, as

expected, higher rain events correspond to an increase in the percent change and possibly increased variability in response of DOC. Correlations between precipitation and DOC and SUVA₂₅₄ are important for management strategy with the predicted increase in precipitation events. Identifying a relationship between these changes and Secchi depth would allow for calculation of estimated losses to be more easily valued.

In this study, changes in Secchi depth from precipitation events were not measured. However, research on a suite of six lakes in Acadia National Park, Maine suggests that mean Secchi depths were shallower by 0.7 to 1.3 m 6 days after a 28 mm storm event. Larger decreases in Secchi depth occurred in clearer lakes (lakes with deeper initial Secchi depths) (Saros, Unpublished data). The function calculated between Secchi depth and percent change in DOC and SUVA₂₅₄ accurately reflects how DOC and SUVA₂₅₄ may change in response to a storm event; however, when the inverse function was explored, DOC and SUVA₂₅₄ did not accurately reflect changes in Secchi depth. Research suggests important relationships between Secchi depth and DOC concentrations. Long term increases in DOC have been documented throughout many lakes in the Northern Hemisphere (Roulet and Moore 2006; Monteith et al. 2007; Zhang et al. 2010). Decreases in water clarity have also been documented in Maine since the mid-1990's (McCullough et al.; Strock et al. 2017). Strock et al. (2017) found that DOC concentration determined the degree to which transparency changed and that rapid changes in climate conditions and patterns of atmospheric deposition have resulted in these shifts in DOC and subsequent declines in water clarity. These strong correlations between DOC and water transparency may have important implications for how lakes respond to precipitation events.

Estimated losses vary depending on initial Secchi depths. Lakes with shallower Secchi depths (2 to 4 m) had higher losses and lakes with deeper Secchi depths (>6 m) had lower losses. Secchi depth changes may vary by storm and by lake, with larger decreases in lakes that have deeper initial Secchi depths from a storm event. The meta-analysis by Ge et al. (2013) incorporates starting water quality value, which accurately accounts for this difference. For example, a 4 m decline in Secchi depth in Sebago lake has a lower WTP than a 1 or 2 m decline in Young Lake and several other lakes. These important distinctions in costs based on initial Secchi value are an additional tool for drinking water management.

High water quality and deeper Secchi depth is important for not only drinking water as we demonstrate in this research, but also is important for recreation, aesthetics, and property value (Wood and Handley 1999; Krysel et al. 2003). For example, for every 1 m loss in Secchi depth, there is a decrease in property value of 15.6 percent (Krysel et al. 2003). A study conducted by Boyle et al. (1997) reveals the largest single source usage of Maine's lakes is associated with clean drinking water based on the number of users. Throughout the state of Maine net economic values, which account for recreational use, lake front properties, and other uses, would be expected to increase by \$2.0 billion if the statewide average minimum water clarity were to increase from 3.78 to 5.15 m. Conversely, a reduction in water clarity from 3.78 to 2.41 m would result in a larger economic loss due to a nonlinear relationship between water clarity and economic activity (Boyle et al. 1997).

This improved understanding of losses for drinking water resources from precipitation events can help identify areas of concern and also help to design appropriate policies to recover maintenance costs, and other water treatment costs (Gadgil 1998).

Another reason it is important to estimate losses is because while households may adapt to use different services, such as treating water at home, this is usually less efficient than collectively provided tap water systems (Whittington et al. 1991) and there are reports that the price per unit of bottled water is often at least 6,000 times more expensive than tap water (Blumenfeld and Leal 2007; EPA 2018). Additionally, higher DOC concentrations from a precipitation event could lead to increases in disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs), among others due to reactions between DOC and disinfectants such as chlorine (Quintiliani et al. 2018). Chlorine is one method to treat drinking water and is generally effective and cheap, therefore identifying how changes in DOC and $SUVA_{254}$ change from storm events and potentially influence estimated losses may aid in treatment strategies. Evaluation of DBPs have been studied for many years, however this research could grow increasingly important if DOC increases from precipitation events.

The results of this study reveal that changes in DOC likely impact estimated losses from reduced water quality by evaluating the relationships between DOC and Secchi depth, and also identifying other lake features that could impact losses. In the meta-analysis by Ge et al. (2013), one of the goals is to identify if different approaches generate the same statistical valuation, and it is acknowledged that lakes may be valued for different types of resources and for different populations of users. Therefore, while the studies in the meta-analysis may value lakes for additional reasons besides only drinking water, the study is designed to account for these differences and still provide a reasonable welfare estimate for a change in water quality for a particular lake regardless of the service provided. Many studies reveal limitations in ecological, economic, and, in particular, combined models (Scheffer et al. 2001; Bateman et al. 2011; Griffiths et al.

2012). This research would be improved by having a better direct link between the ecological data and the economic model, however few studies include how changes in both DOC and SUVA₂₅₄ (an important measurement for drinking water managers) due to changes in climate may affect current and future estimated losses from reductions in water quality.

3.6. Conclusion

Estimating the welfare losses of reductions in water quality is challenging. For this study, we estimated losses based on a WTP function (Ge et al., 2013), and therefore provided lower-bound estimates of the welfare impacts of precipitation events. While insightful, we recognize the limitations of our analysis and acknowledge numerous opportunities for improving assessments of the welfare impacts from changing dissolved organic carbon. First, characterizations of the welfare impacts of precipitation events and changing water quality could be improved by relying on a benefit-transfer approach tailored to this environmental and policy scenario. Improvements could come from a greater reliance on studies focused on similar reductions in water quality (e.g., WTA reductions or WTP to avoid reductions; episodic changes in water quality). The function used in this study to calculate the water quality based on changes in Secchi depth does not reflect the reality of the DOC impacts. The function established by Ge et al. (2013) is very non-linear, while the relationship between DOC and Secchi depth is more linear. Establishing a better function to calculate water quality based on changes in DOC, rather than Secchi depth, and including lake and watershed characteristics important to DOC response and using this in the WTP function will strengthen our estimate of losses from reduced water quality. The precipitation events evaluated in this study are episodic, with drinking water resources returning to pre-storm DOC concentrations relatively quickly;

therefore, cost-effective strategies for certain utilities may involve short-term solutions such as providing bottled drinking water, rather than altering or implementing new treatment strategies. However, this suggestion comes with the caveat that our estimated losses do not correspond with predicted increases in frequency of precipitation events in the future. With these increases in the frequency and severity of storm events, management strategies may need to be altered further.

We remain hopeful that this exploratory research provides useful insights about linking changes in dissolved organic carbon to the welfare impacts of changing water quality. Specifically, this study is useful in that it attempts to find links and identify variables impacting potential losses using a benefit-transfer function that was already developed. This method is more cost effective for identifying potential implications from storm events than primary research. Our research illustrates the steps and analyses required to develop tools that managers could apply using little and readily available data. Managers could also benefit from future research focused on the particular linkages between changing precipitation, dissolved organic carbon, water quality, and household welfare. Such research could improve the function relating Secchi depth and DOC or $SUVA_{254}$ and therefore improve evaluations of how reduced water clarity could contribute to higher variability in DOC response from storm events. Likewise, additional social science research of the welfare impacts of episodic changes in water quality could improve characterizations of the household impacts of and household responses to precipitation events. In closing, we believe combining knowledge of long-term increases in DOC and reduced water clarity with information from this research that suggests depth, residence time, wetland coverage, and DOC and $SUVA_{254}$ contribute to losses

could be very useful knowledge for drinking water treatment managers to ensure high quality drinking water.

CHAPTER 4

DIFFERENCES IN THE EFFECTS OF STORMS ON DISSOLVED ORGANIC CARBON (DOC) IN BOREAL LAKES DURING AN EARLY SUMMER STORM AND AN AUTUMN STORM

4.1. Abstract

In boreal lakes, increased precipitation events have been linked to increased concentrations of dissolved organic carbon (DOC), however the effects of seasonal differences on DOC and how this may impact storm response remain unclear. We evaluated DOC concentration and a set of DOC quality metrics during an early summer storm and an autumn storm on a suite of six lakes in Acadia National Park in Maine, U.S.A. to better understand differences in seasonal storm response. Our results revealed differences in the response of DOC quality metrics to an early summer versus an autumn storm. During the early summer storm, in deep lakes with longer residence times, we found a greater positive response in the ratio of absorption coefficients a_{250} and a_{365} (known as $E_2:E_3$) and spectral slope ($S_{275-295}$), and a greater negative response in Specific Ultraviolet Absorbance ($SUVA_{254}$) and DOC specific absorbance values at 320nm and 380nm (a^*_{320} and a^*_{380}). During the autumn storm, in lakes with large watershed area to lake area ratios, $SUVA_{254}$, a^*_{320} , and a^*_{380} experienced a greater positive response and $S_{275-295}$ and $E_2:E_3$ experienced greater negative response. Land cover was highly correlated with changing DOC quality metrics in the early summer storm but did not play a significant role in the autumn storm response. Our research provides evidence of seasonal differences in the effects of storms on boreal lakes, which are ultimately mediated by a combination of lake and watershed characteristics as well as seasonal changes in climate such as solar radiation and antecedent weather conditions.

4.2. Introduction

Dissolved organic carbon (DOC) is an important regulator of ecosystem structure and function in boreal lakes (Williamson et al. 1999; Tranvik et al. 2009; Brown et al. 2017). DOC affects overall water transparency and thermal stratification (Snucins and Gunn 2000; Solomon et al. 2015), alters pH and alkalinity (Oliver et al. 1983; Evans et al. 2005), impacts microbial production (Tranvik 1992; Wetzel et al. 1995), and attenuates harmful ultraviolet radiation (Morris et al. 1995). Widespread increases in DOC and color in lakes in the Northern Hemisphere have been attributed to a combination of factors including increases in air temperatures (Lepistö et al. 2014; Pagano et al. 2014), changes in the intensity of the hydrological cycle (Weyhenmeyer et al. 2012; Fasching et al. 2016), and reductions in acid deposition (Monteith et al. 2007).

Lakes respond rapidly to external pressures, including changes in weather and climate as well as land use (Aulló-Maestro et al. 2017). In many regions across the globe, precipitation events have increased (Groisman et al. 1999; Jentsch et al. 2008; Donat et al. 2013; Easterling et al. 2017), particularly in the northeastern United States, with a 60-70 percent increase since the 1950's (Madsen and Fidor 2007; Spierre et al. 2010; Madsen and Wilcox 2011; Melillo et al. 2014; Frei et al. 2015; Huang et al. 2017; Huang et al. 2018). Since 1996 the northeastern U.S. has received 53 percent more extreme precipitation events compared to 1901-1995 (Huang et al. 2018). Increased precipitation can lead to changes in water chemistry, nutrient loading, increased particulates, and increased DOC. Studies have examined relationships between rainfall and nutrients (Reichwaldt and Ghadouani 2012; Morabito et al. 2018), but less is known about how changes in precipitation influence DOC. Much of the climate change literature with respect to limnology is dominated by evaluation of long-term and global patterns that

result from atmospheric warming (Woodward et al. 2016), however more recent research investigates the influence of short-term precipitation events on lakes compared to longer-term lake changes from climate change (e.g. Williamson et al. 2014; Williamson et al. 2016). Understanding how DOC responds to precipitation events at different times of the year is still poorly considered.

When considering lakewater DOC response to precipitation events, season is an important feature. For example, an increase in winter precipitation that results in substantial spring runoff may displace a large volume of the lake's volume downstream, therefore old DOC in the lake from previous seasons may be replaced by DOC from the catchment that is more labile compared to other seasons (Hudson et al. 2003). Increases in DOC concentration have been observed in summers with high rainfall (Hudson et al. 2003) particularly after dry periods where the upper soils have been oxidized to produce labile DOC (Dillon and Molot 1997; Tranvik 1998). Antecedent conditions also affect the response of DOC to various climate variables. Gavin et al. (2018) demonstrated an increase in DOC after a heavy precipitation month that had dry antecedent conditions. Increases in DOC concentrations were also noted in Canadian boreal lakes after 90% of mean summer precipitation fell in a four-day rain event (Couture et al. 2012). Both the quantity of precipitation and the season in which the precipitation events occur influence DOC concentrations (Urban et al. 1989; Hudson et al. 2003).

Season also affects lakewater DOC responses in other ways. Incident solar radiation, which varies seasonally, can have profound long- and short-term effects on DOC concentrations in boreal lakes. In one study, over 11 days, approximately 50% of stream DOC was lost under natural light conditions due to photodecomposition (Gennings et al. 2001). In another study, over the course of 12 years, it was estimated that

photodecomposition processes had the potential to remove most of the allochthonous DOC entering lakes (Molot and Dillon 1997). This radiation can impact lake thermal properties such as epilimnion thickness that also may influence DOC response to storm events. Shallower epilimnia in early summer, near the summer solstice, may lead to more photobleaching of DOC, altering DOC quality, while deeper epilimnia in the autumn may lead to less light exposure, less photobleaching, and a different storm response compared to early summer.

The influence of landscape features on lakewater DOC response to storms may also vary seasonally. The ratio of the watershed area to the lake area (WA:LA) is related to DOC concentration and quality (Schindler 1971; Xenopoulos et al. 2003). Additionally, the composition of the watershed, including coverage by wetlands (Dillon and Molot 1997; Temnerud et al. 2014) or amount of forested area (Nguyen et al. 2013; Chen et al. 2016) influences DOC concentration and quality. The influx and processing of DOC into the lake can be altered by residence time (Xenopoulos et al. 2003). Increases in the amount and rate of stream, groundwater, and subsurface inflows into lakes occur from extreme precipitation events (Lee et al. 2007), therefore watershed characteristics can contribute to flushing of DOC from upper soil horizons into lakes (Hinton et al. 1997). Depending on the amount of precipitation during a particular time of year, these landscape features around lakes are also important for evaluating the impacts of storm events on changing DOC.

The timing of precipitation events is also changing seasonally. Average annual precipitation across the U.S. has increased by 4 percent since 1901 with this increase attributed to more precipitation during the autumn season (Easterling et al. 2017). In the northeastern U.S. specifically, precipitation has increased by more than 15 percent in the

autumn and by about 3 percent in the spring since 1901 (Easterling et al. 2017), with the months of September and October contributing the most to increased extreme precipitation events due to an increase in the frequency of extreme events caused by tropical cyclones (Huang et al. 2018). This variation in precipitation at different times of year may impact lake response to storm events, specifically DOC.

The goal of this study was to investigate relationships between the quantity and quality of lakewater DOC and the seasonal timing of precipitation events. Does DOC respond differently to a rain event in the early summer compared to a rain event in the autumn? To address this question, a set of DOC concentration and quality metrics were measured during storm events in June and October of 2016 in six boreal lakes located in Acadia National Park, Maine, USA. We evaluated changes in DOC concentration and changes in DOC quality using metrics that represent the balance of allochthonous inputs, photobleaching, and bacterial processing. Each lake was sampled 1-2 days prior to the storm, and 1-2 days as well as 4 days after a rain event.

4.3. Methods

4.3.1. Study site and lake selection

The lakes in this study are located in Acadia National Park in Maine, USA (Figure 4.1; Table 4.1). Within the 35,000-acre park, lakes cover approximately 2,600 acres. Granite dominates the landscape throughout the park and soils in Acadia are derived from granite and schist tills (Gilman et al. 1988). Spruce-fir forests, representative of the northern boreal forest, cover much of the landscape in Acadia with stands of oak, maple, and beech, typical of the eastern deciduous forest, dominant in some areas that were burned in a fire in 1947.

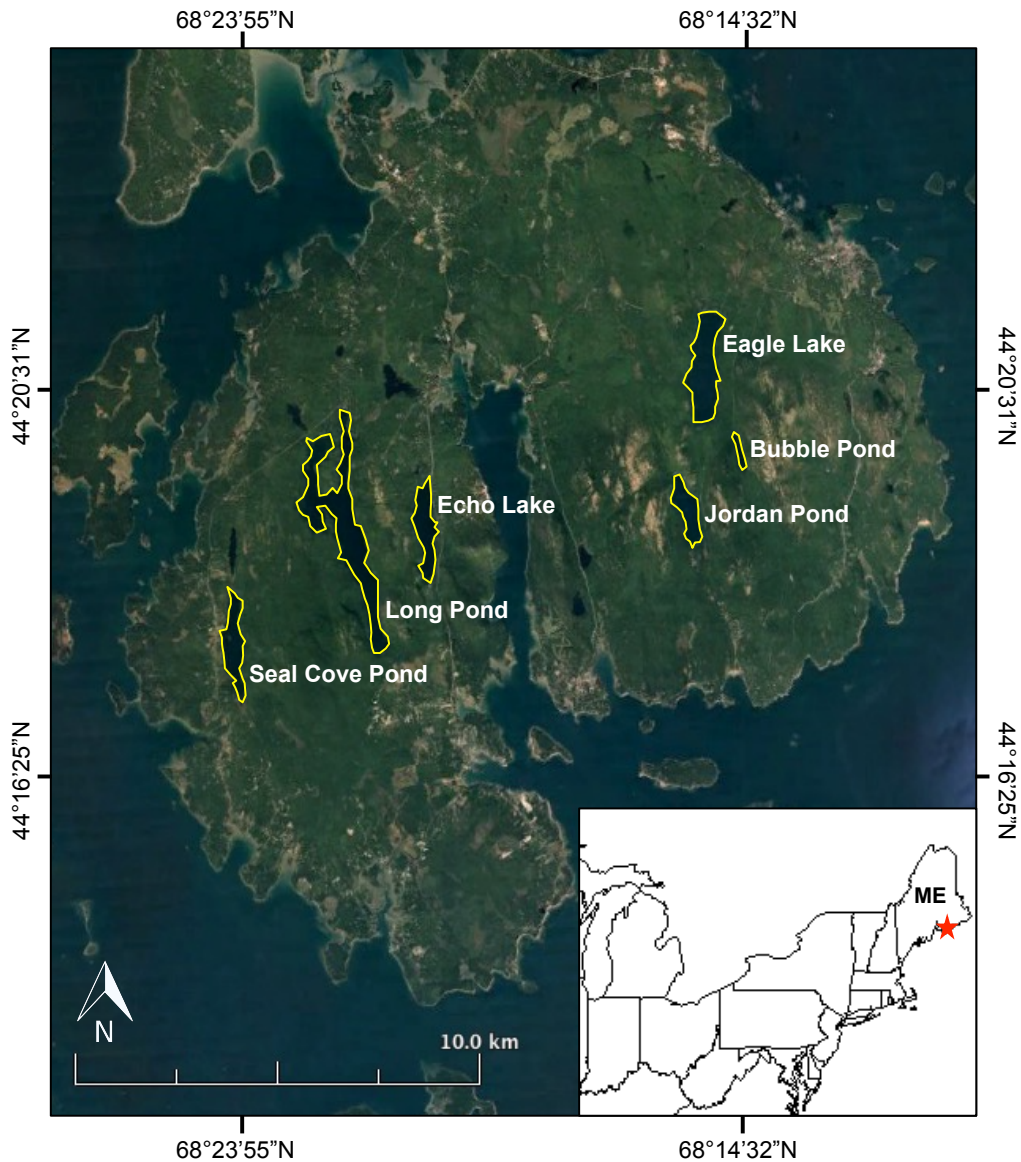


Figure 4.1. Map of the study area in Acadia National Park, Maine, USA. The 6 study lakes are outlined in yellow.

We selected a suite of six lakes in Acadia National Park to conduct our study. Prior research has revealed that DOC concentrations have increased over the past two decades (Strock et al. 2017) in these six lakes. DOC concentrations ranged from 1.9 to 4.7 mg L⁻¹ (Table 4.1). Lake sizes, measured in surface area, ranged from 0.1 to 3.8 km², and maximum lake depth ranged from 12 to 46 m (Table 4.1). Residence time ranged from 0.5 to 5.9 years, and the ratio of the watershed area to lake (surface) area (WA:LA) ranged from 3 to 13.5 (Table 4.1).

Table 4.1. Select characteristics of the 6 study lakes.

Lake	Watershed Area (km²)	Lake Area (km²)	Watershed Area: Lake Area	Volume (×10⁶ m³)	Maximum Depth (m)	Residence Time (years)	Mean DOC (mg L⁻¹)
Jordan	4.0	0.8	5.3	17.0	46	5.9	1.9
Bubble	1.8	0.1	13.5	0.6	12	0.5	2.3
Eagle	5.6	1.9	3.0	22.4	34	3.8	2.1
Echo	5.1	1.0	5.3	6.2	20	1.6	3.0
Long	13.1	3.8	3.4	33.4	34	3.1	3.1
Seal Cove	7.6	1.0	7.3	3.9	13	0.5	4.7

4.3.2. Storm events and sample collection

We sampled two events, one in June and one in October, representing an early summer rain event and an autumn rain event. Precipitation and air temperature data were collected from the Acadia National Park McFarland Hill (ACAD-MH) weather station. Hourly climate data were converted to daily climate data from October 1, 2015 to October 31, 2016. These events had 25.9 mm of rain within 24 hours in June and 30.2 mm of rain in 24 hours in October (Figure 4.2). The goal of the study was to evaluate the response of extreme precipitation events, which is typically defined as a set amount in a 24-hour period (i.e. Karl et al. 1995; Kunkel et al. 2003; Spierre et al. 2010; Fernandez et al. 2015; and others) or events that fall into the highest 1 to 2 percent of all precipitation events for a given year or range of years. While these rain amounts may not be considered extreme rain events, these storms still constituted the top rain events for the year, falling into the top 2.2% of highest rainstorms between May 1, 2016 and October 31, 2016.

Samples were collected at each lake at 3 time periods for each storm: 1-2 days before (Pre), 1-2 days after (P1), and 4 days after (P2) the rain events (Table 4.2). Water was collected from the epilimnion using a van Dorn bottle at each lake for analysis of DOC concentration and quality metrics.

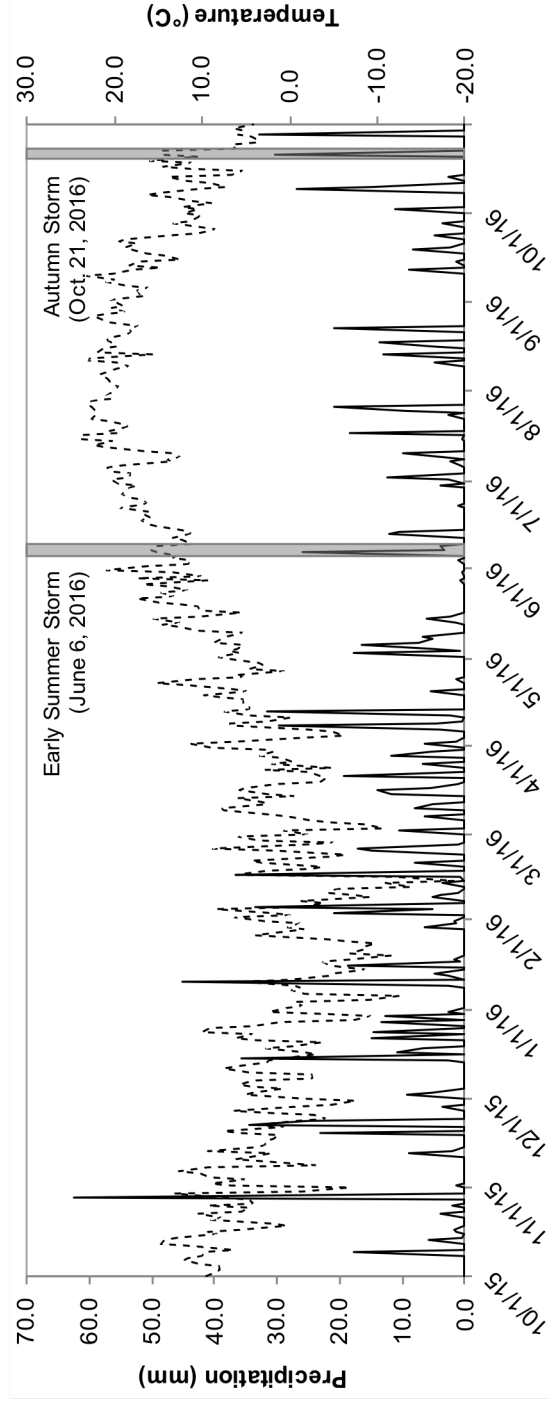


Figure 4.2. Total daily precipitation in mm and mean daily temperature in °C for the water year. Measurements are from October 1, 2015 through October 31, 2016. Precipitation is indicated by the solid line, temperature is indicated by the dashed line, and gray bars indicate the two storms.

Table 4.2. Dates of storms and sampling events for the 6 lakes.

	Storm Dates	Sampling Dates		Storm Total Precipitation (mm)
		Pre	P1 P2	
<i>Early Summer</i>	June 6, 2016	June 4, 2016	June 7, 2016 June 10, 2016	25.9
<i>Autumn</i>	October 21, 2016	October 19, 2016	October 23, 2016 October 25, 2016	30.2

4.3.3. Analysis of DOC concentration and absorbance properties

All samples were analyzed for DOC concentration and quality immediately upon receipt. DOC samples were filtered through Whatman GF/F filters pre-rinsed with deionized water. DOC concentration was analyzed on a Shimadzu Total Organic Carbon Analyzer (Shimadzu Corporation, Kyoto, Japan). A Varian Cary UV-VIS spectrophotometer was used to measure the absorbance properties within 200-800 nm wavelengths to assess DOC quality. Corrected absorbance values were calculated by subtracting a Milli-Q deionized water blank from the raw absorbance values. The following equation was used to calculate Napierian dissolved absorption coefficients (Helms et al. 2008; Kirk 2011):

$$a_d = \frac{2.303 \times D}{r}$$

where D is the decadal optical density value from the spectrophotometer and r (measured in meters) is the path length of the quartz cuvette. Specific Ultraviolet Absorbance (SUVA₂₅₄), a^*_{320} , and a^*_{380} were calculated by dividing a_d by the DOC concentration (mg L⁻¹). Napierian coefficients were used to evaluate the ratio of a_{250} to a_{365} (known as $E_2:E_3$). To calculate spectral slopes over the 275-295 nm range ($S_{275-295}$), linear regression was used to estimate the slope of the relationship between $\ln a_d$ and wavelength, expressed as a positive number. SUVA₂₅₄ correlates strongly with aromaticity (Weishaar et al. 2003), providing an indication of the source and biological availability of the DOC. Increases in a^*_{320} are driven by inputs of terrestrially derived DOC that introduces less photobleached DOC and may decrease transparency (Helms et al. 2008). CDOM may be represented by a^*_{380} which absorbs ultraviolet light and visible light (Helms et al. 2008), is primarily responsible for optical properties, and plays an

important role in shielding biota from harmful UV radiation (Walsh et al. 2003). $E_2:E_3$ tracks changes in the relative size of DOC molecules. This ratio is negatively related to average molecular DOC weight and positively correlated with low molecular weight DOC compounds, therefore the ratio increases with UV light processing and decreases in response to bacterial DOC processing (Berggren et al. 2018). DOC photobleaching largely drives increases in $S_{275-295}$ (Helms et al. 2008) which indicates increases in exposure to sunlight. These DOC quality metrics were used to evaluate the response to storm events and reflect the balance of allochthonous inputs, photobleaching, and bacterial processing.

Percent change of DOC concentration, $SUVA_{254}$, a^*_{320} , a^*_{380} , $E_2:E_3$, and $S_{275-295}$ was calculated for the early summer and autumn storms. P1 and P2 samples were each normalized to the Pre sample: Percent change = $((\text{PostX} / \text{Pre}) - 1) * 100$, where X is the P1 or P2. Percent change values less than zero indicate a decrease in that metric, positive values indicate an increase, and zero indicates no change. Percent change values were used in all data analyses.

4.3.4. Land cover data

Land cover data were measured using the National Elevation Dataset from the United States Geological Survey (Table 4.3). The United States Geological Survey 2011 dataset was used to collect national land cover data (NLCD). Slope was calculated using digital elevation models collected from the Maine Office of GIS.

Table 4.3. Landscape characteristics for each of the 6 lakes.

Lake	Slope (degrees)	Landcover (%)						
		Developed	Deciduous	Evergreen	Mixed Forest	Scrub- Shrub	Herbaceous	Wetlands
Jordan	47.5	6.2	10.0	34.7	13.6	24.7	8.2	2.6
Bubble	17.7	3.2	7.8	48.0	15.3	17.6	4.6	3.6
Eagle	45.1	12.0	9.8	34.3	29.4	8.4	1.6	4.6
Echo	23.4	9.8	1.1	64.4	17.8	1.8	1.4	3.6
Long	27.7	3.4	3.5	64.2	17.5	2.4	0.4	8.6
Seal Cove	17.1	4.1	0.8	59.2	16.9	4.8	3.2	11.0

4.3.5. Data analysis

To assess differences in the mean response of DOC concentration, $SUVA_{254}$, a^*_{320} , a^*_{380} , $E_2:E_3$, and $S_{275-295}$ between Pre and P2 for each storm and between early summer and autumn across all six lakes, one-way analysis of variance (ANOVA) was used. Levene's test for homogeneity and Shapiro-Wilks normality test were used to test for the assumptions of ANOVA. A significance level of $p < 0.05$ was used.

Pearson's correlation coefficient was used to evaluate correlations between the percent change of DOC metrics (DOC concentration, $SUVA_{254}$, a^*_{320} , a^*_{380} , $E_2:E_3$, and $S_{275-295}$) and select lake characteristics (surface area, volume, maximum depth, WA:LA, and residence time) for each storm. A significance level of $p < 0.10$ was used. Pearson's correlation coefficient was also used to evaluate correlations between the percent change of DOC metrics (DOC concentration, $SUVA_{254}$, a^*_{320} , a^*_{380} , $E_2:E_3$, and $S_{275-295}$) and landcover for both storms. A significance level of $p < 0.05$ was used. Adjustment for multiple comparisons to correct for false comparisons was not used in order to capture more correlations and observe any differences between periods and seasons in this initial study. All statistical analyses were co conducted using R software (version 3.3.2, The R Foundation for Statistical Computing, 2016).

4.4. Results

4.4.1. Comparisons of mean responses across lakes and seasons

Across lakes, the mean response of DOC concentration to the early summer and autumn storms did not differ ($p = 0.99$), however the mean responses of DOC quality metrics were different between the two seasons ($p < 0.01$). The percent changes in $SUVA_{254}$, a^*_{320} , and a^*_{380} decreased in response to the early summer storm, whereas they increased after the autumn storm (Figure 4.3). $SUVA_{254}$ decreased by 3.8 ± 1.4 percent in

the early summer and increased by 6.6 ± 1.8 percent in the autumn ($p = 0.004$, Figure 4.3b). The percent change for a^*_{320} and a^*_{380} decreased by 6.6 ± 1.8 and 15.0 ± 4.3 respectively in the early summer and increased by 14.8 ± 5.7 and 29.1 ± 11.2 in the autumn ($p = 0.005$, $p = 0.008$, Figure 4.3c-d). The percent change of $E_2:E_3$ and $S_{275-295}$ was opposite of $SUVA_{254}$, a^*_{320} , and a^*_{380} , increasing in the early summer and decreasing in the autumn. $E_2:E_3$ increased by 11.4 ± 2.1 percent in the early summer and decreased by 11.0 ± 5.7 percent in the autumn ($p = 0.002$, Figure 4.3e). $S_{275-295}$ increased by 4.7 ± 0.8 percent in the early summer and decreased by 3.0 ± 1.8 percent in the autumn ($p = 0.003$, Figure 4.3f). Detailed information for pre-storm values, and percent change for P1 and P2 in early summer and autumn seasons for each of the six study lakes individually can be found in Appendix B (Table. B.1; Figure B.1).

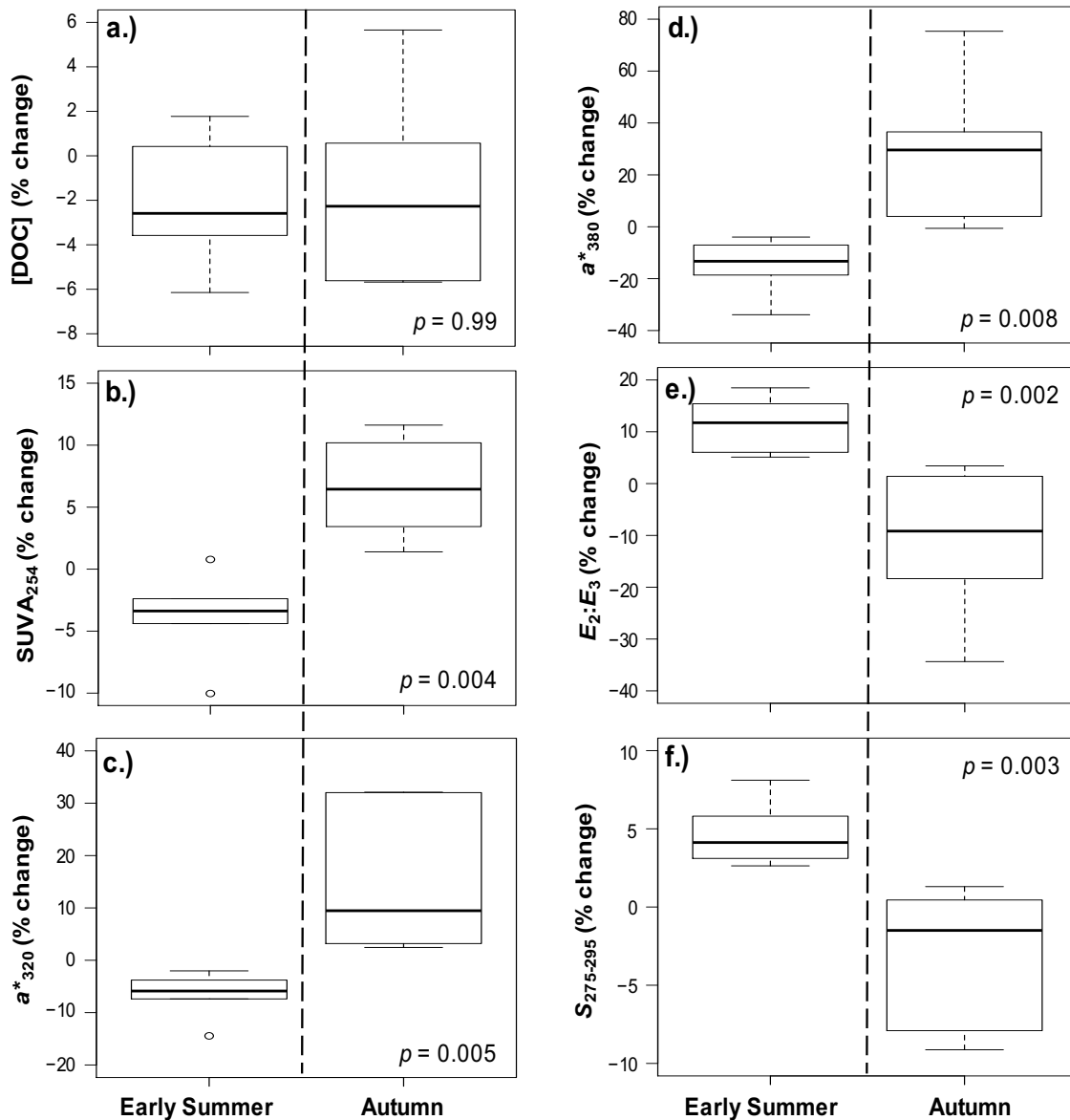


Figure 4.3. Mean responses of DOC metrics during Early Summer versus Autumn storms. The mean responses of the six study lakes are for a.) [DOC], b.) SUVA₂₅₄, c.) a^*_{320} , d.) a^*_{380} , e.) $E_2:E_3$, and f.) $S_{275-295}$ of Early Summer versus Autumn storms represented by percent change from Pre to P2 (n=6). The p values indicate differences between Early Summer and Autumn.

4.4.2. Correlations between DOC metrics and lake characteristics

Correlations between percent change of DOC metrics suggest differences between seasons and post-storm periods. In the early summer, DOC concentration was negatively correlated to $SUVA_{254}$, a^*_{320} , and a^*_{380} during both P1 and P2, while in the autumn DOC concentration was negatively correlated to $SUVA_{254}$, a^*_{320} , and a^*_{380} during P1 and positively correlated during P2 (Figure 4.4). In the early summer, DOC concentration was not strongly correlated to $E_2:E_3$ or $S_{275-295}$ during P1 and positively correlated during P2, and in the autumn DOC concentration was also not strongly correlated to $E_2:E_3$ or $S_{275-295}$ during P1 and negatively correlated during P2 (Figure 4.4). Correlations among DOC concentration and DOC quality metrics appeared stronger during the P2 period compared to P1. Significant correlations during each season and time period vary. In the early summer during the P2 period, there was a negative correlation between DOC concentration and $SUVA_{254}$ ($r = -0.91$, $p = 0.01$; Figure 4.4b) and a positive correlation between DOC concentration and $E_2:E_3$ ($r = 0.83$, $p = 0.04$, Figure 4.4b). In the autumn during the P2 period, there was a negative correlation between DOC concentration and $S_{275-295}$ ($r = -0.82$, $p = 0.04$, Fig. 4d).

Correlations between lake characteristics and the percent change of DOC metrics to storms differed between seasons. Overall, during the early summer there were more correlations between percent change in DOC metrics and residence time and depth, while in the autumn there were more correlations between percent change in DOC metrics and WA:LA. During the early summer for the P2 sampling, across the six lakes, there were significant negative correlations between residence time and changes in $SUVA_{254}$ ($r = -0.76$, $p = 0.08$), a^*_{320} ($r = -0.84$, $p = 0.04$), and a^*_{380} ($r = -0.76$, $p = 0.06$) and between maximum depth and changes in a^*_{320} ($r = -0.75$, $p = 0.08$, Figure 4.4b; Table 4.4).

During the same early summer P2 period, there were significant positive correlations between changes in $S_{275-295}$ and maximum depth ($r = 0.77, p = 0.07$) and residence time ($r = 0.85, p = 0.03$, Figure 4.4b; Table 4.4). During the autumn for the P1 sampling, there were significant positive correlations between changes in a^*_{320} and WA:LA ($r = 0.84, p = 0.04$) and between changes in $E_2:E_3$ and maximum depth ($r = 0.80, p = 0.05$) and residence time ($r = 0.76, p = 0.08$, Fig. 4c; Table 4). During the autumn P1 period, there was a negative correlation between changes in $S_{275-295}$ and WA:LA ($r = -0.74, p = 0.09$, Figure 4.4c; Table 4.4). In the P2 sampling for the autumn storm, there was a significant positive correlation between changes in DOC concentration and WA:LA ($r = 0.76, p = 0.08$, Figure 4.4d; Table 4.4). Although only significant for the early summer P2 sampling, during all sampling periods, changes in $SUVA_{254}$, a^*_{320} , and a^*_{380} were negatively correlated with maximum depth and residence time (Figure 4.4). Correlations for changes in $E_2:E_3$ and $S_{275-295}$ were variable across seasons and sample periods (Figure 4.4).

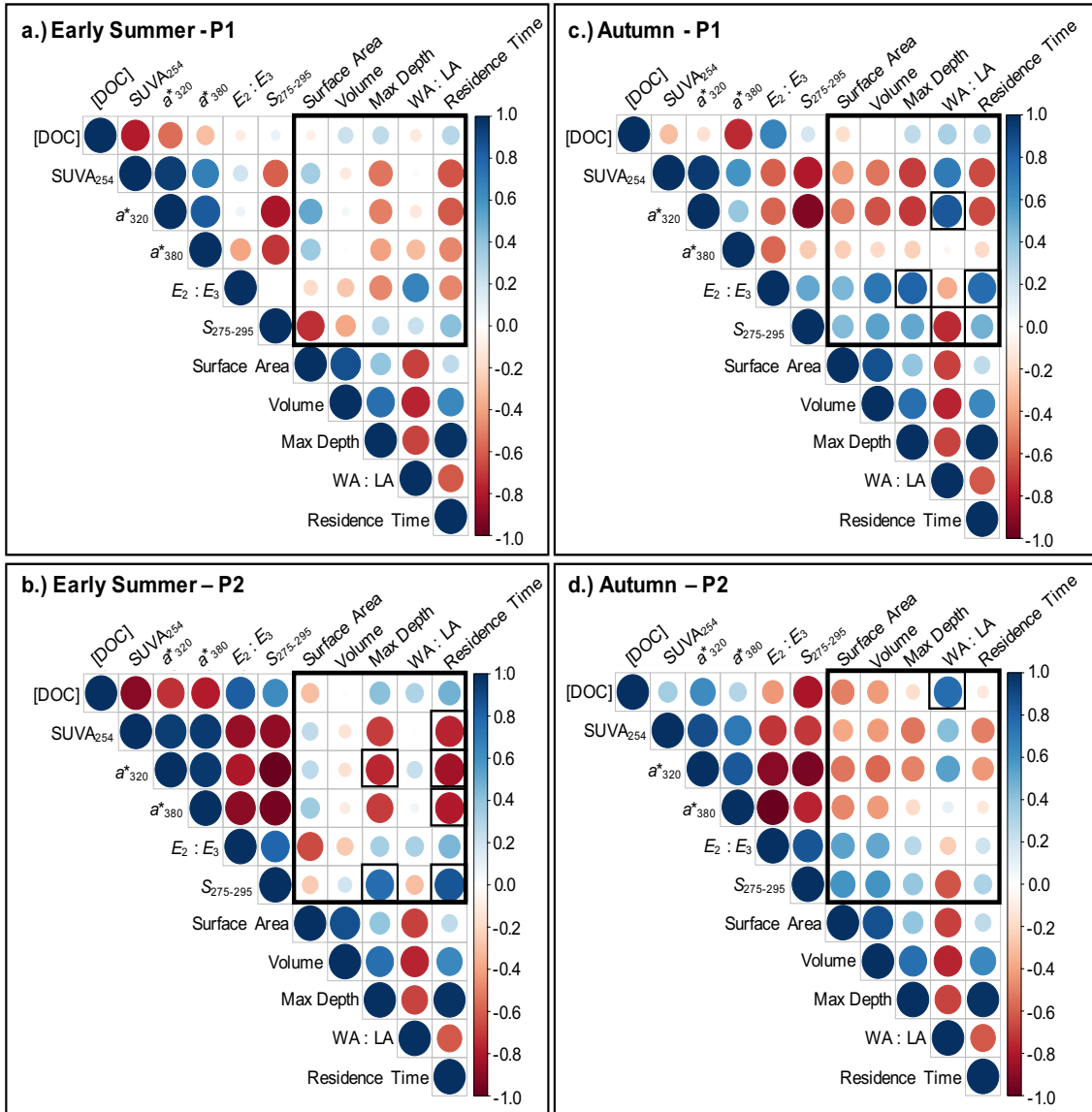


Figure 4.4. Correlations between DOC metrics and select lake characteristics. Correlations are between the percent change of [DOC], SUVA₂₅₄, a^*_{320} , a^*_{380} , $E_2 : E_3$, $S_{275-295}$ and select lake characteristics (outlined in the larger boxes) during the Early Summer for a.) P1 and b.) P2 and Autumn c.) P1 and d.) P2 storm samplings. Smaller boxes (within the larger boxes) indicate significant relationships ($p < 0.10$) between DOC metrics and lake characteristics. WA:LA indicates the ratio of watershed area to lake area

Table 4.4. Correlation (r) and p values for significant correlations between DOC metrics and select lake characteristics. Correlation (r) and p values are between [DOC], $SUV_{A_{254}}$, a^*_{320} , a^*_{380} , $E_2:E_3$, and $S_{275-295}$ and select lake characteristics ($p < 0.10$) during P1 and P2 storm samplings for Early Summer and Autumn storms. Italics indicate a negative relationship.

DOC Metric	Early Summer		Autumn	
	<i>P1</i>	<i>P2</i>	<i>P1</i>	<i>P2</i>
[DOC]				WA:LA ($r = 0.76$; $p = 0.08$)
$SUV_{A_{254}}$		<i>Residence Time</i> ($r = -0.76$; $p = 0.08$)		
a^*_{320}		<i>Max Depth</i> ($r = -0.75$; $p = 0.08$)	WA:LA ($r = 0.84$; $p = 0.04$)	
		<i>Residence Time</i> ($r = -0.84$; $p = 0.04$)		
a^*_{380}		<i>Residence Time</i> ($r = -0.79$; $p = 0.06$)		
$E_2:E_3$			Max Depth ($r = 0.80$; $p = 0.05$)	
			Residence Time ($r = 0.76$; $p = 0.08$)	
$S_{275-295}$		Max Depth ($r = 0.77$; $p = 0.07$)	WA:LA ($r = -0.74$; $p = 0.09$)	
		Residence Time ($r = 0.85$; $p = 0.03$)		

4.4.3. Correlations between DOC metrics and land cover

Correlations between land cover variables and the percent change of DOC metrics differed between early summer and autumn. Various correlations were significant during the early summer for the P1 and P2 sample period, however there were no significant correlations between land cover and DOC metrics during either of the autumn storm samplings (Figure 4.5). During the early summer P1 period changes in $SUVA_{254}$, a^*_{320} , a^*_{380} were negatively correlated with deciduous land cover ($r > -0.89$, $p < 0.02$), and positively correlated with evergreen land cover ($r > -0.87$, $p < 0.03$; Figure 4.5a). During the same period, change in $SUVA_{254}$ was positively correlated with wetlands ($r = 0.87$, $p = 0.03$) and changes in a^*_{320} and a^*_{380} were negatively correlated with scrub-shrub ($r > -0.87$, $p < 0.03$; Figure 4.5a). Change in $S_{275-295}$ was positively correlated with scrub-shrub ($r = 0.83$, $p = 0.04$) and with herbaceous land cover ($r = 0.90$, $p = 0.01$; Figure 4.5a). During the early summer P2 period, there were some consistencies between changes in $SUVA_{254}$, a^*_{320} , a^*_{380} and land cover and some changes in correlations for $E_2:E_3$ and $S_{275-295}$. Change in a^*_{380} was again negatively correlated with deciduous land cover ($r = -0.82$, $p = 0.04$), positively correlated with evergreen land cover ($r = 0.82$, $p = 0.04$), and negatively correlated with scrub-shrub ($r = -0.85$, $p = 0.03$; Figure 4.5b). Change in $E_2:E_3$ was positively correlated with scrub-shrub ($r = 0.88$, $p = 0.02$) and negatively correlated with wetlands ($r = -0.88$, $p = 0.02$; Figure 4.5b); and changes in $S_{275-295}$ had a positive correlation with slope ($r = 0.88$, $p = 0.02$; Figure 4.5b).

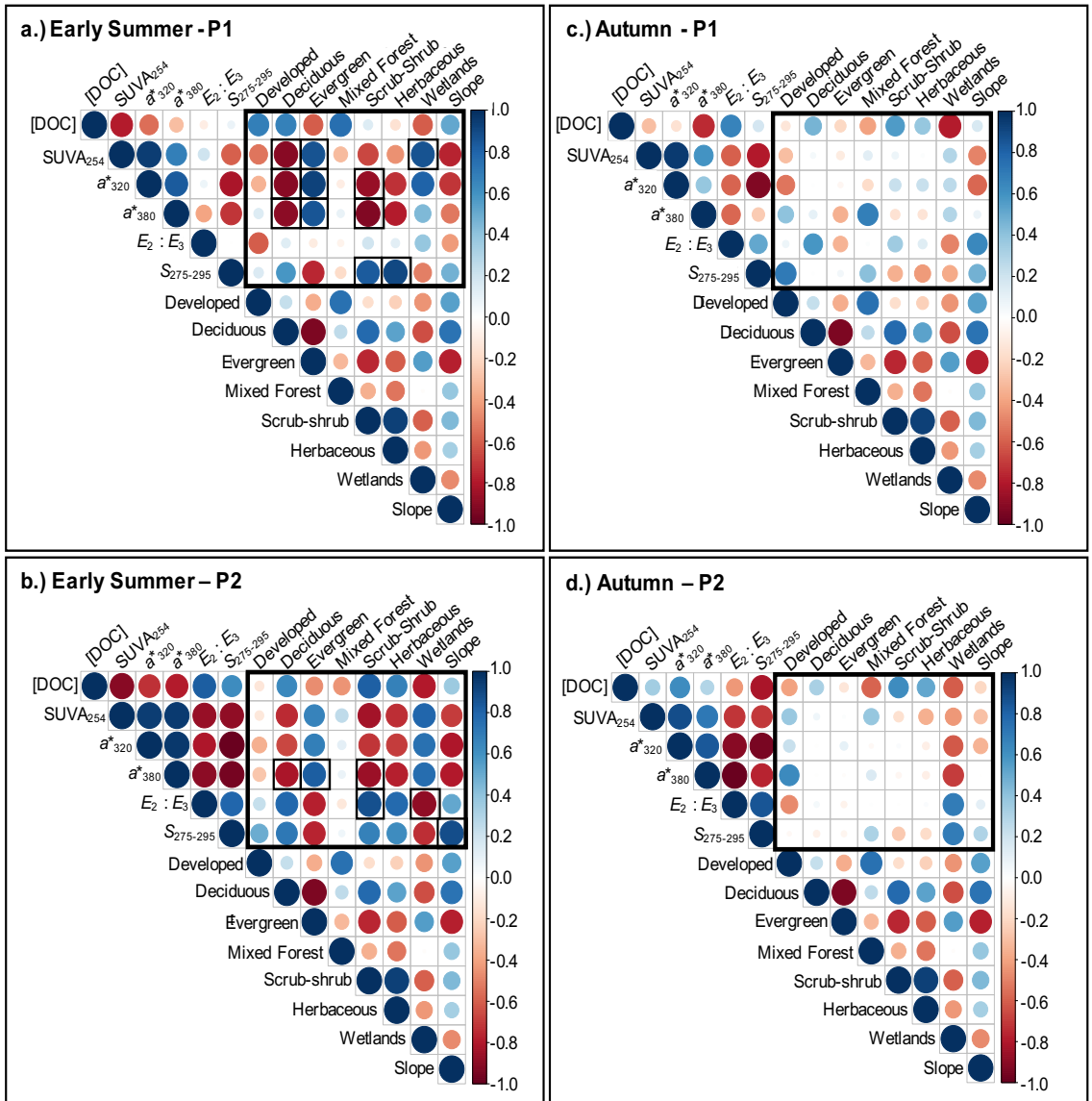


Figure 4.5. Correlations between DOC metrics and land cover. Correlations are between the percent change of [DOC], SUVA₂₅₄, a^*_{320} , a^*_{380} , $E_2:E_3$, and $S_{275-295}$ land cover (outlined in the larger boxes) during the Early Summer for a.) P1 and b.) P2 and Autumn c.) P1 and d.) P2 storm samplings. Smaller boxes around circles (within the larger boxes) indicate significant relationships ($p < 0.05$) between changes in DOC metrics and land cover.

4.5. Discussion

Our results reveal seasonal differences in the response of DOC quality metrics to storm events in boreal lakes, while response of mean DOC concentration for the six lakes was similar across seasons. Our analyses suggest that the response of DOC quality metrics to storms was mediated by differing lake and watershed characteristics in the early summer versus autumn. In the early summer storm, deep lakes with longer residence times experienced a greater positive response in $E_2:E_3$ and $S_{275-295}$, and a greater negative response in $SUVA_{254}$, a^*_{320} , and a^*_{380} . In the autumn storm, lakes with large WA:LA ratios experienced a greater positive response in $SUVA_{254}$, a^*_{320} , and a^*_{380} and a greater negative response in $E_2:E_3$ and $S_{275-295}$ (Figure 4.6). The balance of the response of DOC quality metrics during the early summer storm suggest photobleaching was the dominant process, whereas the balance of the response of DOC quality metrics during the autumn storm suggest increased allochthonous inputs and bacterial processing were the dominant processes contributing to change. Land cover was more highly correlated with changing DOC quality metrics in the early summer storm and did not play a significant role in the autumn storm response. Our results indicate that there are seasonal differences in the effects of the early summer and the autumn storm.

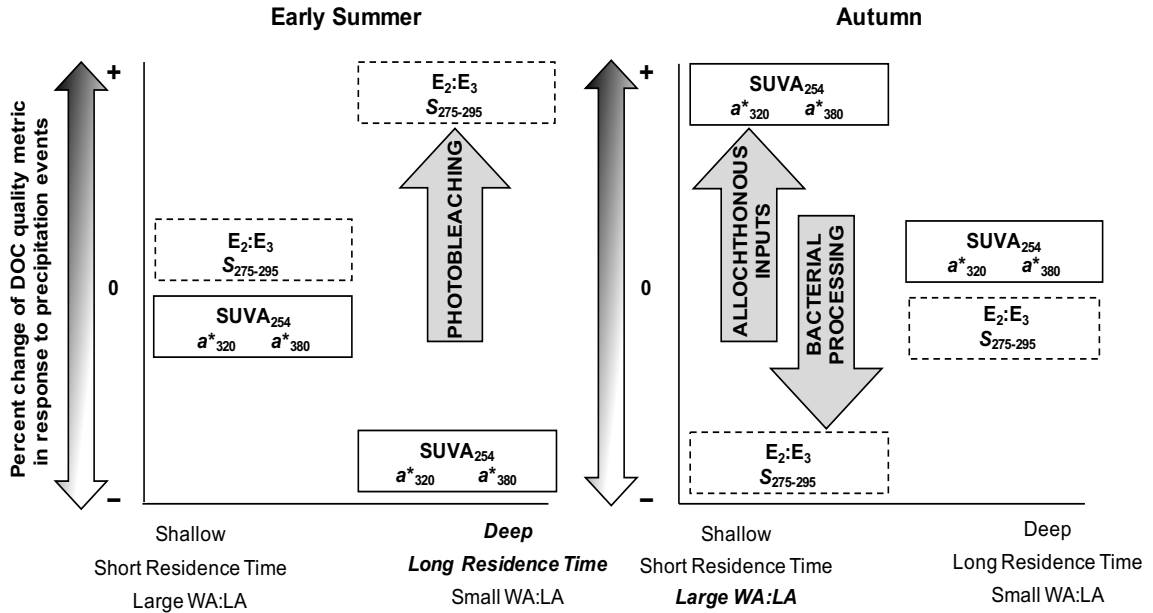


Figure 4.6. Conceptual figure of the dominant processes contributing to changes in DOC quality metrics for the Early Summer and Autumn storms. All responses are indicated by the percent change in DOC quality to a precipitation event, and the lake characteristics that influence a particular response. $E_2:E_3$ and $S_{275-295}$ are indicated by dashed boxes and $SUVA_{254}$, a^*_{320} , and a^*_{380} are indicated by solid boxes. Gray arrows indicate dominant processes that contribute to DOC quality response and bold italics indicate key lake characteristics.

In the early summer storm event, solar radiation and dry antecedent weather conditions likely contributed to the observed increases in $E_2:E_3$ and $S_{275-295}$ and decreases in $SUVA_{254}$, a^*_{320} , and a^*_{380} . In early summer, exposure to solar radiation was higher and the epilimnion was shallower than in the autumn. These factors would contribute to increased photobleaching which contributes to the processing and degradation of DOC as it flows through the system (Aulló-Maestro et al. 2017), ultimately contributing to a rapid loss of allochthonous DOC and increased transparency and may influence the observed positive response of DOC quality metrics representative of within-lake processes during this period. This response was largely observed in deep lakes with long residence times. Longer residence time likely resulted in more extensive exposure to sunlight (Vachon et al. 2016). The deep lakes with longer residence times had increases in $S_{275-295}$ suggesting more photobleaching occurred during this season (Helms et al. 2008; Aulló-Maestro et al.

2017). The positive response of $E_2:E_3$ supports increased photobleaching during this early summer period, as an increase in this ratio suggests an increase in UV light processing (Berggren et al. 2018). The role of residence time in storm response is important as it correlates to the loading of fresh DOC and determines the history of DOC exposure to light, which can influence the photosensitivity of DOC (Vachon et al. 2016). Conversely, DOC quality metrics indicative of allochthonous inputs decreased in response to the early summer storm. Dry antecedent conditions to the early summer storm may contribute to more increased photobleaching, rather than an influx of terrestrially derived, or allochthonous, DOC. Key functions of DOC, including the effects on water transparency and attenuation of harmful ultraviolet radiation, may be altered by storm events and have subsequent negative effects on aquatic ecosystem structure and function.

During the autumn storm event, wetter conditions, decay of organic matter in the watersheds from spring to autumn, and reduced solar radiation may have contributed to the observed increases in $SUVA_{254}$, a^*_{320} , and a^*_{380} decreases in $E_2:E_3$ and $S_{275-295}$. This response was largely observed in lakes with a larger WA:LA ratio. A larger watershed area allows for more decomposition on the landscape and this organic matter is then flushed into the lakes by autumn storms. Increased a^*_{320} results from these fresh inputs of terrestrial DOC (Helms et al. 2008; SanClements et al. 2012) and reduced photobleaching. Allochthonous DOC is often less biolabile (Willamson et al. 2014), therefore with increased storminess, particularly in the autumn months, increased terrestrially derived DOC could have important implications for aquatic ecosystems. Reduced exposure to sunlight results in decreased photobleaching, and the negative correlation between changes in $S_{275-295}$ and WA:LA supports increased allochthonous inputs that introduce non-photobleached DOC (Hargreaves 2003). Additionally, a

reduction in the ratio of $E_2:E_3$ suggests an increase in bacterial DOC processing (Berggren et al. 2018). This bacterial processing corresponds to the decay or breakdown of plant matter in the watersheds, which can then be flushed into lakes during storm events, contributing to the vulnerability of lake ecosystems to changing DOC quality with increased frequency of storm events.

During the early summer storm, land cover is more highly correlated with changes in DOC quality metrics, whereas it does not play a significant role in the autumn. The negative correlation between changes in $SUVA_{254}$, a^*_{320} , and a^*_{380} and deciduous cover corresponds to a strong negative response or decrease in these DOC quality metrics in response to storm events. Lake watersheds with more deciduous cover and less evergreen cover have a greater negative response in DOC quality metrics to storm events than lake watersheds with more evergreen cover in the early summer. Measured DOC concentration is often higher in soils under coniferous forests than DOC measured in soils under deciduous forests (Khomotova et al. 2000). Additionally, the percent of deciduous cover was low across all watersheds, therefore in the autumn, there was likely a negligible effect of deciduous forest similar to boreal streams in northern Sweden, where the presence of deciduous forest had a negligible effect on DOC during the wet period (Ågren et al. 2007). Thus, in the autumn storm, the size of the watershed contributes to larger inputs of terrestrial matter or allochthonous material, regardless of forest type. In the early summer storm, the positive correlation between changes in $S_{275-295}$ and slope support the larger positive response of DOC quality metrics in the deep lakes with higher residence time, as these lakes' watersheds also have the steepest slopes. Relationships between DOC quality and land cover contribute to the explanation of seasonal variability in lake response to storm events.

DOC quality metrics can be highly responsive to changes in precipitation, temperature, and solar radiation. Hudson et al. (2003) evaluated DOC data over 21 years in a set of lakes in Canada and found that solar radiation explained 50% of the variation in DOC concentration across seasons. In a shallow lake in Hungary, DOC exports from the catchment were driven by both the availability of flushable terrestrial carbon and the seasonality of precipitation, which is also a common pattern in many temperate and boreal lakes (Aulló-Maestro et al. 2017). Additionally, research by Aulló-Maestro et al. (2017) supports that photobleaching plays a key role in the processing and degradation of DOC during times of high solar radiation. This processing of DOC by photobleaching can influence carbon cycling and also increase the transparency of the water column (Osburn et al. 2009) as well as change optical properties (Yamashita et al. 2013). This supporting evidence, among others, paired with our research, suggests correlations between optical properties and lake characteristics as well as land cover may provide us with the knowledge to produce a framework for how DOC in lakes respond to storm events. Although this study provides only a small snapshot and would not encompass all seasonal differences, it supports literature on how DOC quality metrics can be a powerful tool to examine lake response and also contributes to understanding potential implications from storm events.

Storms may contribute to increased variability of seasonal DOC. While DOC quality fluctuates seasonally, storm events may introduce additional variability, and potentially cause abrupt changes in lake ecosystems. It has been acknowledged that the relationship between DOC concentrations and precipitation over multiple years is variable and inconsistent, therefore suggesting that long-term climate change and acidification in addition to weather events are driving changing trends in DOC (Gavin et

al. 2018). The effect of weather events on changes in DOC is being increasingly researched, however few studies attempt to explain the specific differences in seasonal DOC quality metrics and how this may impact storm response.

This research provides insight into key differences between lakewater DOC response to an early summer versus an autumn storm. In the early summer storm, the response of the DOC quality metrics suggests that photobleaching was the primary process contributing to the observed changes in deep lakes with long residence times. In the autumn storm, the response of the DOC quality metrics suggests that more allochthonous inputs and increased bacterial processing were the primary processes contributing to the observed changes in lakes with large WA:LA ratios (Figure 4.6). Changes in climate such as solar radiation and antecedent weather conditions, that lead to subsequent changes in lake thermal structure, also influence DOC response to storm events. With storm events predicted to increase in frequency and intensity, particularly in the autumn months, increased variability in lakewater DOC metrics may be expected in the future.

CHAPTER 5

HOW DOES CHANGING ICE-OUT AFFECT ARCTIC VERSUS BOREAL LAKES? A COMPARISON USING TWO YEARS WITH ICE-OUT THAT DIFFERED BY MORE THAN THREE WEEKS

5.1. Abstract

The timing of lake ice-out has advanced substantially in many regions of the Northern Hemisphere, however the effects of ice-out timing on lake properties and how they vary regionally remain unclear. Using data from two inter-annual monitoring datasets for a set of three Arctic lakes and one boreal lake, we compared physical, chemical and phytoplankton metrics from two years in which ice-out timing differed by at least three weeks. Our results revealed regional differences in lake responses during early compared to late ice-out years. With earlier ice-out, Arctic lakes had deeper mixing depths and the boreal lake had a shallower mixing depth, suggesting differing patterns in the influence of the timing of ice-out on the length of spring turnover. Differences in nutrient concentrations and dissolved organic carbon between regions and ice-out years were likely driven by changes in precipitation and permafrost thaw. Algal biomass was similar across ice-out years, while cell densities of key *Cyclotella sensu lato* taxa were strongly linked to thermal structure changes in the Arctic lakes. Our research provides evidence that Arctic and boreal regions differ in lake response in early and late ice-out years, however ultimately a combination of important climate factors such as solar insolation, air temperature, precipitation, and, in the Arctic, permafrost thaw, are key drivers of the observed responses.

5.2. Introduction

Lakes throughout the Northern Hemisphere are experiencing changes in the timing of ice-on, ice-out and the duration of ice cover (Kuusisto 1987; Schindler et al. 1990; Livingston 2000; Magnuson et al. 2000; Futter 2003). Changes in the timing of ice-out are of particular interest for understanding plankton dynamics, as ice-out marks the onset of spring conditions and the period leading to the peak of the growing season. Ice-out timing also has stronger direct connection to climate change than ice-on because individual lake properties influence the freezing process more strongly than the thawing process (Spoka et al. 2006; Adrian et al. 2009). The timing of ice-out has advanced substantially, occurring up to 21 days earlier over the past 40 to 100 years at mid-latitudes (Weyhenmeyer et al. 2005; Jensen et al. 2007; Beier et al. 2012; Benson et al. 2012) and up to 13 days earlier since 2000 in the Arctic (Smejkalova et al. 2016).

Correlations suggest that the timing of ice-out is an important driver of phytoplankton community structure and biomass. Paleolimnological studies have inferred that earlier ice-out has triggered changes in lake properties that caused shifts in diatom communities at both high and mid-latitudes and that the taxon-specific shifts occurred earlier in Arctic lakes (ca. 1870) than in boreal lakes (ca. 1970) due to expansion of planktonic diatom habitat and lengthening of the growing season (Rühland and Smol 2005; Rühland et al. 2008; Rühland et al. 2015). Specifically, it has been hypothesized that shorter periods of ice cover induced by warming air temperatures favor small *Cyclotella* taxa due to increased water column stability throughout the growing season (Smol and Douglas 2007; Rühland et al. 2015). However, based on neo- and paleolimnological approaches, small *Cyclotella sensu lato* taxa can be more abundant during early (Rühland et al. 2008; Wiltse et al. 2016) or late (Boeff et al. 2016; Kienel et

al. 2017) ice-out years. Similarly, monitoring of a boreal lake over a 14-year period and a temperate lake over a 15-year period both revealed that the timing of ice-out does not clearly influence total phytoplankton biomass during the growing season (Meis et al. 2009; Peltomaa et al. 2013). Collectively, these studies reveal that the links between ice-out and phytoplankton dynamics vary in pattern and strength across systems.

This regional variation is well illustrated by comparing Arctic and boreal lakes. The rate of warming is at least twice the global average at high Arctic latitudes above 60° North compared to other latitudes (McBean 2005; Screen and Simmonds 2010; Jeong et al. 2014), which will influence seasonal light patterns, the length of the growing seasons, timing of ice-out relative to phytoplankton blooms (Peeters et al. 2007) and the onset of stratification (Livingstone 2008) differently than at lower latitudes that contain boreal regions. The relationship between air temperature and the actual timing of ice-out is also not linear among different latitudes and differs greatly between Arctic and boreal regions within the Northern Hemisphere (Weyhenmeyer et al. 2004). With both Arctic and boreal regions experiencing rapid climate change, questions remain regarding the magnitude of effect between the regions. In Arctic lakes, ice-out occurs between May to July depending on latitude, while in boreal lakes it occurs between March to May. Therefore, Arctic lakes experience a shorter ice-free season during which there is higher light exposure and rapid onset of stratification shortly after ice-out compared to boreal lakes, which have a longer spring turnover period, longer growing season and a gradual increase in light exposure and temperatures. These differences suggest that the strength of effects of changes in the timing of ice-out may differ between Arctic and boreal lakes.

Changes in ice-out are an important physical change in lake ecosystems and there are several potential pathways by which the timing of ice-out can affect phytoplankton

ecology (Figure 5.1). These pathways, however, are not only affected by the timing of ice-out but also by other climatic factors including precipitation, wind and cloud cover (i.e. incoming solar radiation). For example, while there are assertions in much of the limnological literature that earlier ice-out will lead to earlier onset and strengthening of thermal stratification (DeStasio et al. 1996; Peeters et al. 2002; Douglas et al. 2004), there is not extensive evidence to support an exclusive relationship. Dependent on elevation, precipitation can be more influential than temperature in driving ice-out (Preston et al. 2016). However, the timing of ice-out is also strongly related to air temperatures in the month or two prior to ice breakup (Livingstone 2000; Beyene 2015), and these months vary by region, with ice-out dates in mid-latitudes reflecting February to March air temperatures and at higher latitudes April to May air temperatures. While air temperatures during those months will be important for lake stratification via effects on ice-out timing, many additional factors (e.g. air temperatures during open water months, wind, cloud cover, water clarity) will affect thermal stratification patterns, potentially weakening any links with ice-out timing. Changes in the length of spring turnover and the length of the open water season are additional physical changes in lake ecosystems that are altered by climatic factors and affect phytoplankton ecology through similar pathways (Figure 5.1). Earlier ice-out will likely lengthen spring turnover and increase the length of the open water season, potentially altering phytoplankton growth and succession (Kienel et al. 2017). A subsequent physical implication from earlier ice-out and changes in thermal stratification and the length of the open water season, is a change in light exposure (Figure 1). The light environment plays an important role in phytoplankton abundance and composition (Peltomaa et al. 2013) and will change variably in boreal and Arctic regions based on changes in ice-out timing, thus clear links between ice-out timing

and light climate are still being investigated. It is also important to note that under-ice algal growth is greater than previously understood (Hampton et al. 2017), raising questions about the extent to which earlier ice-out will strongly affect seasonal phytoplankton dynamics.

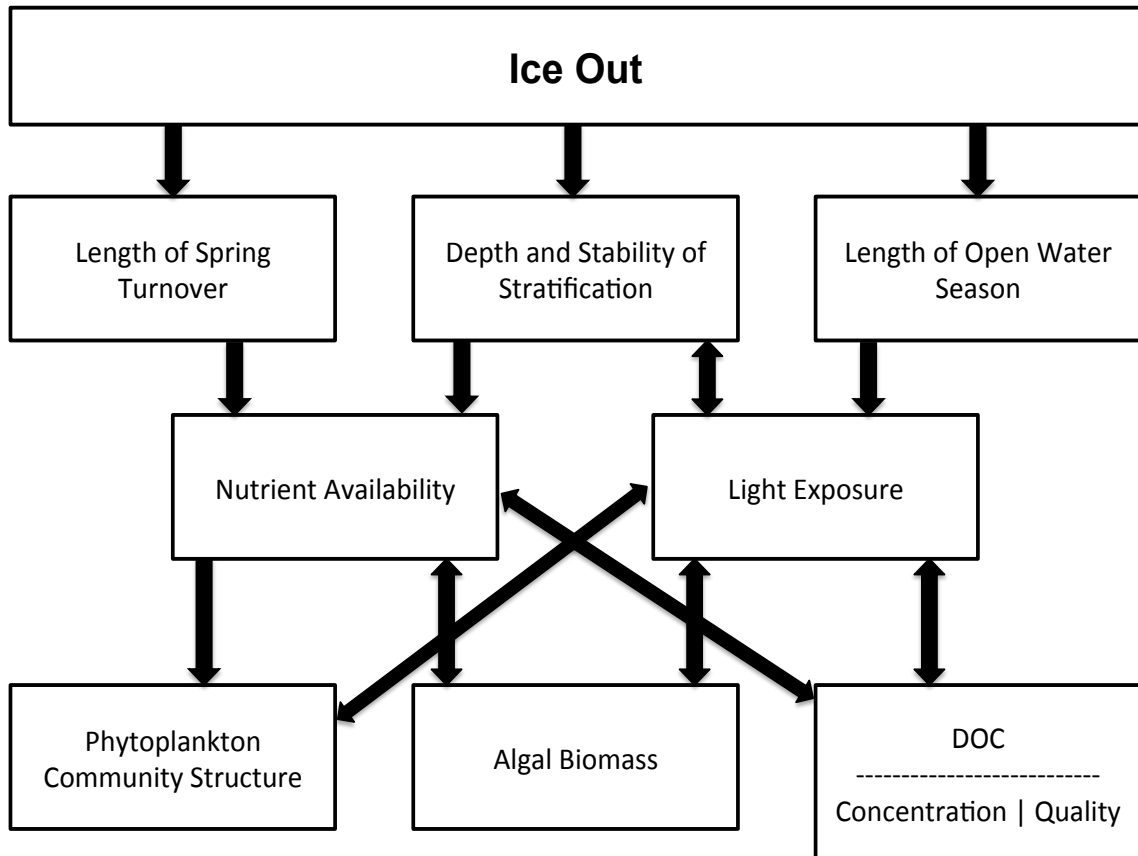


Figure 5.1. Conceptual diagram of a subset of the potential effects of ice-out on lake ecosystems.

These pathways that drive physical changes in lake ecosystems may also contribute to chemical changes that influence phytoplankton (Figure 5.1). Earlier ice-out may lead to increased nutrient loading (De Senerpont Domis et al. 2013), or conversely, reductions in the duration of winter ice cover may contribute to reduced under-ice nitrate production (Powers et al. 2017), thus links between ice-out and changes in nutrients remain unclear. In addition, increased light exposure from earlier ice-out can alter

dissolved organic carbon concentrations and quality (Cory et al. 2014). It is important to note that changes in ice-out have effects on chemical pathways in lakes, but that climate factors also influence chemical pathways independent of ice-out. For example, in the Arctic, warming promotes thawing of permafrost, which may increase nutrient loading to lakes (Levine and Whalen 2001) and further affect aquatic ecosystems, making it important to distinguish links between ice-out and phytoplankton to better resolve how future climate will alter aquatic ecosystems.

To address the extent to which ice-out affects phytoplankton dynamics requires a better understanding of how spring and summer lake conditions vary between early and late ice-out years and how they compare in different regions. How different are lake conditions in an early versus late ice-out year? To improve mechanistic understanding of the influence of ice-out on Arctic and boreal lake ecosystems, we evaluated the effects of ice-out timing on thermal stratification and differences in biological and biogeochemical characteristics in an early and late ice-out regime. We analyzed data from two inter-annual monitoring datasets, one from the Arctic (a set of 3 lakes in West Greenland) and one from the boreal zone (a lake in Maine, USA). These datasets were collected over multiple years to assess changing lake conditions over time and were originally collected for two different studies. We chose two years from each of these datasets for which monitoring data were available and that had the largest differences in ice-out dates (Table C.1). Ice-out timing differed by at least three weeks and we compared a suite of physical, chemical and phytoplankton metrics between the years in each area.

5.3. Methods

5.3.1. Study design

To compare the responses of Arctic and boreal lakes to the timing of ice-out, we used data from two inter-annual monitoring datasets that were originally collected for two different studies. In the Arctic, a set of three lakes was monitored, while in the boreal region, one lake was monitored. For the boreal lake, we chose two years from the dataset in which ice-out timing differed by 41 days (2012 early ice-out and 2015 late ice-out; Table 5.1). Data were available for both years to compare lake parameters during late spring (hereafter referred to simply as spring), as well as during the peak of summer stratification (hereafter referred to as summer). For the Arctic lakes, data were available to compare spring lake parameters during two years in which ice-out timing differed by 30 days (2016 early ice-out and 2015 late ice-out; Table 5.1). Summer data were not available for 2015 but were available for 2013, a year in which ice-out was 22 days later than in 2016 (Table 5.1). As a result, for the Arctic lakes, the comparisons of spring lake parameters are from one set of years (2016 versus 2015) and for a different set of years (2016 versus 2013) for summer responses. This limits our ability in the Arctic lakes to address questions about whether ice-out effects on spring conditions are sustained into summer. Ice-out dates for the Arctic and boreal regions from 2010 to 2016 can be found in Appendix C.

Table 5.1. Dates of comparison for early ice-out versus late ice-out years in Arctic and boreal ecosystems. Comparisons were also made in the late spring (denoted Spring) and in mid-summer during peak thermal stratification (denoted Summer). Range of dates for Arctic includes sampling at all 3 lakes.

Region	Spring		Summer		
		Early ice-out	Late ice-out	Early ice-out	Late ice-out
Arctic	Year	2016	2015	2016	2013
	Ice-out date	18 May	17 June	18 May	9 June
	Sampling dates	28–30 June	27 June–1 July	15–17 July	19–21 July
Boreal	Year	2012	2015	2012	2015
	Ice-out date	19 March	29 April	19 March	29 April
	Sampling dates	11 June	11 June	12 July	10 July

5.3.2. Site description

The Arctic lakes in this study are located adjacent to Kangerlussuaq, southwest Greenland, which is situated within the Arctic Circle and spans from the Greenland Ice Sheet to midway to the coast (Figure 5.2). Soils are derived from weathered granidioritic gneisses (Nielsen 2017) and vegetation is variable but consists largely of woody shrubs around the lakes in this study. Continuous permafrost underlies the region (Nielsen 2017) and surface inflow and outflow are not typically apparent (Hasholt and Anderson 2003). Mean summer temperature is 10.2 °C from June to August and precipitation averages 173 mm per year (Saros et al. 2016). Ice-out typically occurs between late May and late June with thermal stratification occurring very quickly thereafter (Brodersen and Anderson 2000). This region contains approximately 20,000 lakes that are mostly chemically dilute and oligotrophic (Anderson et al. 2001). The three lakes selected for this study are all located in the Kellyville region to the east of Kangerlussuaq (Table 5.2). The lakes are generally small and similar in depth and surface area (Table 5.2). These lakes are not fed by the Greenland Ice Sheet, therefore turbidity is low.

The boreal lake in this study, Jordan Pond, is located in Acadia National Park in Maine, USA (Figure 5.2; Table 5.2). Lakes in Acadia National Park cover 2,600 acres of

the approximately 35,000-acre park. Soils in Acadia are derived from granite and schist tills, and granite dominates the landscape throughout the park (Gilman et al. 1988). Representative of northern boreal forest, spruce-fir forests persist in Acadia with stands of oak, maple and beech dominant in some areas that were burned in a fire in 1947. Data from Acadia National Park's weather station suggests average summer temperature from June through August is 19 °C and average annual precipitation is 1,455 mm. Ice-out timing is variable but typically occurs between late March and late April. Jordan Pond is an oligotrophic lake with a maximum depth of 45 m and is somewhat larger than the Arctic lakes in this study.

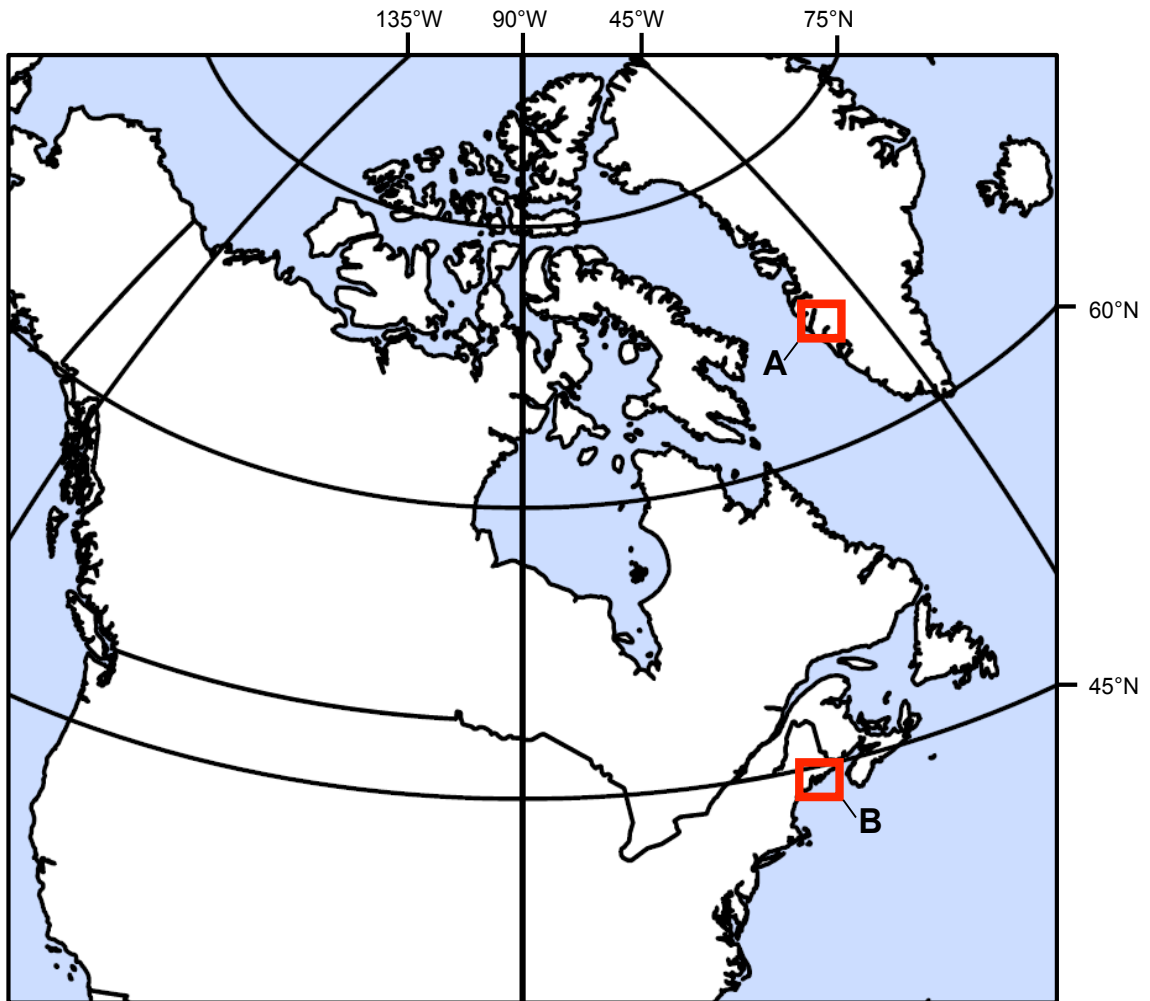


Figure 5.2. Map depicting the location of the (A) Arctic and (B) boreal study sites.

Table 5.2. Select characteristics of the 4 study lakes.

Region	Lake	Lat	Long	Elevation (m)	Surface Area (km ²)	Volume (×10 ⁶ m ³)	Max Depth (m)
Arctic	SS2	66.99	-50.96	190	0.368	2.49	12
	SS85	66.98	-51.06	195	0.246	0.94	11
	SS1590	67.01	-50.98	200	0.243	1.16	18
Boreal	Jordan	44.33	-68.26	83	0.800	17.4	45

5.3.3. Climate variables

Air temperature and precipitation data for Jordan Pond were collected from the Acadia National Park McFarland Hill (ACAD-MH) weather station. Air temperature and precipitation data for Kangerlussuaq and the Arctic lakes were collected from the Kangerlussuaq airport (DMI 04231) weather station.

5.3.4. Comparative lake sampling

5.3.4.1. Physical

Sampling across all four of the study lakes was conducted using the same methods during each of the dates listed in Table 1. Secchi depth was measured on the shady side of the boat using a black and white disc. Temperature profiles consisted of measurements at each meter down to 25 m using a YSI EXO2 Sonde (Xylem Inc., Yellow Springs, OH, USA). Epilimnion thickness was calculated based on temperature profiles and defined as the first depth at which there was ≥ 1 °C change per meter. Water column stability (Schmidt stability) was calculated from temperature profiles and lake bathymetry using the rLakeAnalyzer package in R [44]. The onset of stratification for the boreal lake was determined as the first day there was a ≥ 1 °C difference per meter in the water column.

5.3.4.2. Chemical

Water was collected from the epilimnion, metalimnion and hypolimnion using a van Dorn bottle at each lake for analysis of total phosphorus (TP) and dissolved inorganic

nitrogen (DIN), which is the sum of nitrate (NO_3^-) and ammonium (NH_4^+). For analysis of DIN, NO_3^- and NH_4^+ , samples were filtered through Whatman GF/F filters pre-rinsed with deionized water. Flow injection analysis using the phenate ($\text{NH}_4\text{-N}$) and cadmium reduction ($\text{NO}_3\text{-N}$) methods (APHA 2000) on a Lachat Quikchem 8500 (Hach Company, Loveland, CO, USA) flow injection analyzer (FIA) were used to quantify NO_3^- and NH_4^+ . TP was determined from whole-water samples using persulfate digestion followed by the ascorbic acid method on a Lachat Quickchem 8500 (Hach Company, Loveland, CO, USA) flow injection analyzer (APHA 2000). After analysis, TP and DIN samples from the epilimnion, metalimnion and hypolimnion were averaged for comparison. Nutrient limitation status was identified by the ratio of DIN:TP, with DIN:TP < 1.5 indicating N limitation, DIN:TP > 3.4 indicating P limitation and values from 1.5 to 3.4 suggesting co-limitation (Bergström 2010).

Water from the epilimnion was used for analysis of dissolved organic carbon (DOC) concentrations and specific ultraviolet absorbance at 254 nm (SUVA_{254}). All DOC concentration and SUVA_{254} samples were filtered through Whatman GF/F filters pre-rinsed with deionized water. A Shimadzu Total Organic Carbon Analyzer (Shimadzu Corporation, Kyoto, Japan) was used to analyze DOC concentrations and a Varian Carey UV-VIS spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) was used to analyze SUVA_{254} by measuring dissolved absorbance property at 254 nm. To provide corrected dissolved absorbance values, a Milli-Q deionized water blank was subtracted from the raw absorbance values and Napierian dissolved absorption coefficients were calculated using the following equation (Helms et al. 2008):

$$a_d = \frac{2.303 \times D}{r}$$

where D is the decadal optical density value from the spectrophotometer and r (measured in meters) is the path length of the quartz cuvette. The DOC-specific absorption coefficient, $SUVA_{254}$, was calculated by dividing a_d (254 nm) by the DOC concentration (mg C L^{-1}).

5.3.4.3. Biological

Water was also collected from the epilimnion, metalimnion and hypolimnion at each lake using a van Dorn bottle to determine phytoplankton biomass (as chlorophyll a). Chlorophyll samples from each depth were filtered through 25 mm Whatman GF/F filters, wrapped in aluminum foil and frozen until analysis. All chlorophyll a samples were analyzed within three weeks of filtration and processed using standard methods (APHA 2000). Filters were ground and 90% acetone was used to extract chlorophyll overnight, then samples were centrifuged and a Varian Cary UV-VIS spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) was used to analyze chlorophyll a concentrations. After analysis, chlorophyll a values from all three depths were averaged on each date to capture a water column average.

We also assessed the response of key diatom taxa that are demonstrated indicators of climate-driven lake ecosystem changes. The relative abundances of *Cyclotella sensu lato* taxa are often correlated with changes in the timing of ice-out (Rühland et al. 2015) and mechanistically have been linked to thermal structure (Saros et al. 2012). Two 50-mL centrifuge tubes were collected from the epilimnion, metalimnion and hypolimnion from each of the four study lakes on all sample dates. In the boreal lake, phytoplankton samples were available for many dates over the two years of interest; we present results across the entire study period for this lake to demonstrate how the two focal spring and summer dates fit into the full seasonal pattern for this lake. All samples were preserved

with Lugol's solution, settled in Utermohl chambers and counted using a Nikon Eclipse TS-100 (Nikon Instruments Inc., Tokyo, Japan) inverted microscope at 400× magnification.

5.3.5. Data analysis

To evaluate patterns in lake metrics in each region, responses of the three Arctic lakes were averaged (mean ± standard error) on each date. Qualitative comparisons were made across all data, as the limited sample size and the unequal number of sites between the two regions did not provide enough power to conduct more advanced statistical analyses.

5.4. Results

5.4.1. Arctic region

In the Arctic lakes, ice-out occurred 30 days earlier in 2016 (18 May) compared to 2015 (17 June) and 22 days earlier compared to 2013 (9 June). Air temperatures differed between early and late ice-out years. During the early ice-out year, monthly average air temperatures were 6.9 to 13.7 °C higher from January to April with the biggest temperature differences in March (10.5 °C higher) and April (13.7 °C higher) compared to the 2015 late ice-out year (Figure 5.3). Average May temperature was 3.7 °C higher in the early ice-out year compared to the 2015 late ice-out year (Figure 5.3). Air temperatures in the early ice-out year were 0 to 1.5 °C higher from January to March compared to the 2013 late ice-out year (Figure 5.3). The largest temperature differences between the early ice-out year and the 2013 late ice-out year were in April (4.7 °C higher) and May (5.5 °C higher). Air temperatures were similar in June and July between the early ice-out year and the 2013 and 2015 late ice-out years (Figure 5.3).

Precipitation varied among early and late ice-out years. Precipitation during the early ice-out year was 2 mm lower in each month from January to April, however in May precipitation was 11 mm higher in the early compared to the 2015 late ice-out year (Figure 5.3). During the early ice-out year, precipitation in June was 3 mm higher and precipitation in July was 5 mm lower than the 2015 late ice year (Figure 5.3).

Precipitation from January to April was lower in the early ice-out year compared to the 2013 late ice-out year with precipitation differences ranging from 0 to 10 mm less (Figure 5.3). During the early ice-out year, May precipitation was 5 mm higher and in June precipitation was 10 mm higher compared to the 2013 late ice-out year. In July, precipitation was 39 mm lower in the early ice-out year compared to the 2013 late ice-out year (Figure 5.3).

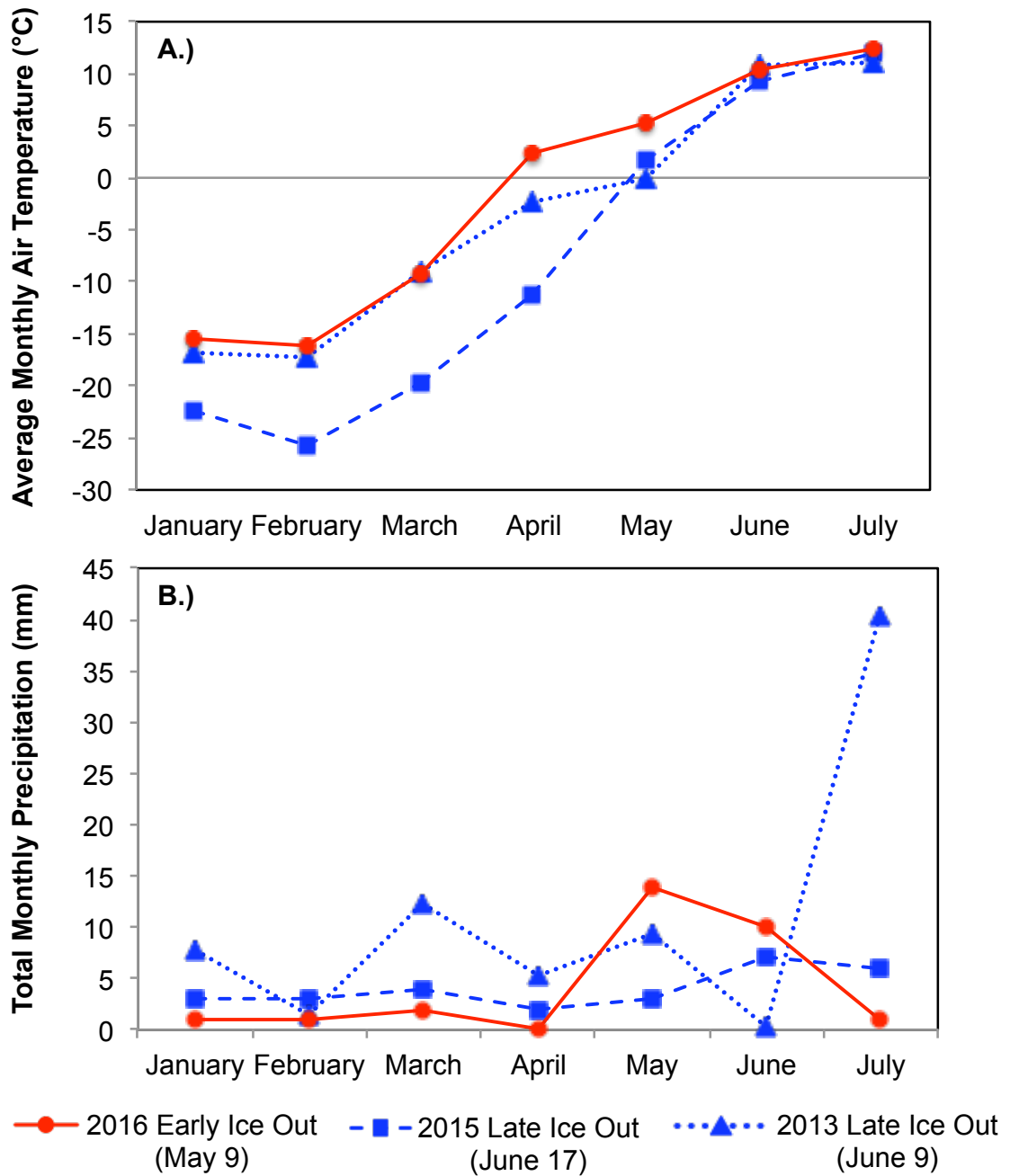


Figure 5.3. Arctic (A) average monthly air temperature in °C and (B) total monthly precipitation in mm for early and late ice-out years.

5.4.1.1. Comparison of spring response across early and late ice-out years

Physical variables of lakes differed in spring between the two years. Water temperature at 2 m was 1.4 °C lower during the early ice-out year compared to the late ice-out year (2015; Figure 5.4). In the early ice-out year, mixing depths were deeper and water clarity was greater compared to the late ice-out year, with epilimnion thickness 2.3 m greater and Secchi depth 2.3 m deeper in the early ice-out year compared to the late ice-out year (Figure 5.4). Water column stability was 20 J m⁻² lower during the early ice-out compared to late ice-out year.

Differences across biogeochemical metrics in Arctic lakes in the spring season were variable across early and late ice-out years. DIN and TP had opposite responses in the spring for the two ice-out years. DIN was 5 µg N L⁻¹ lower and TP was 3 µg P L⁻¹ greater in the early ice-out year compared to the late ice-out year. DIN:TP was 1.7 (indicative of co-limitation by N and P) in the early ice-out year compared to 13 (indicative of P limitation) in the late ice-out year (Figure 5.4). DOC concentration was higher in the early ice-out year by 6.8 mg L⁻¹ and SUVA₂₅₄ was higher by 1.6 mg C L⁻¹ m⁻¹ during early ice-out compared to late ice-out (Figure 5.4).

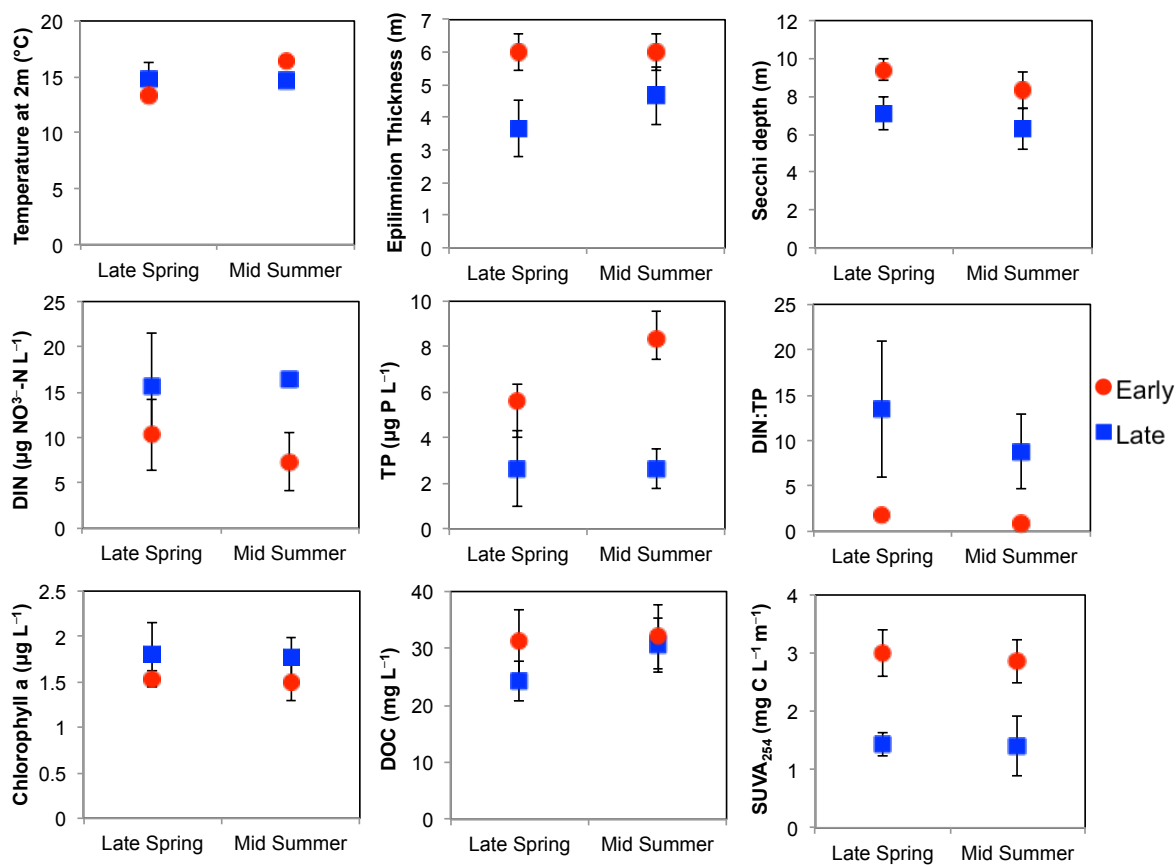


Figure 5.4. Comparison of lake metrics for early and late ice-out conditions during the spring and summer in Arctic lakes. Responses of the three Arctic lakes are averaged (mean \pm standard error) on each date. For the 2016 early ice-out year, spring sampling occurred from 28–30 June and summer sampling was conducted from 15–17 July. For late ice-out years, spring sampling occurred from 27 June–1 July 2015 and summer sampling was conducted from 19–21 July 2013.

In terms of algal response, algal biomass was similar in early and late ice-out years. Average integrated chlorophyll *a* concentration was $0.3 \mu\text{g L}^{-1}$ lower in the early ice-out compared to the late ice-out year (Figure 5.4). Diatom cell densities of the three centric species were different in spring for early and late ice-out years. *D. stelligera* was three times lower in the early ice-out year (by 55 cells mL^{-1}) compared to late ice-out. *L. bodanica* was $1.6 \text{ cells mL}^{-1}$ higher in the early ice-out year compared to the late ice-out year. *L. radiosa* was five times lower (29 cells mL^{-1}) in the early ice-out year compared to late ice-out (Figure 5.5).

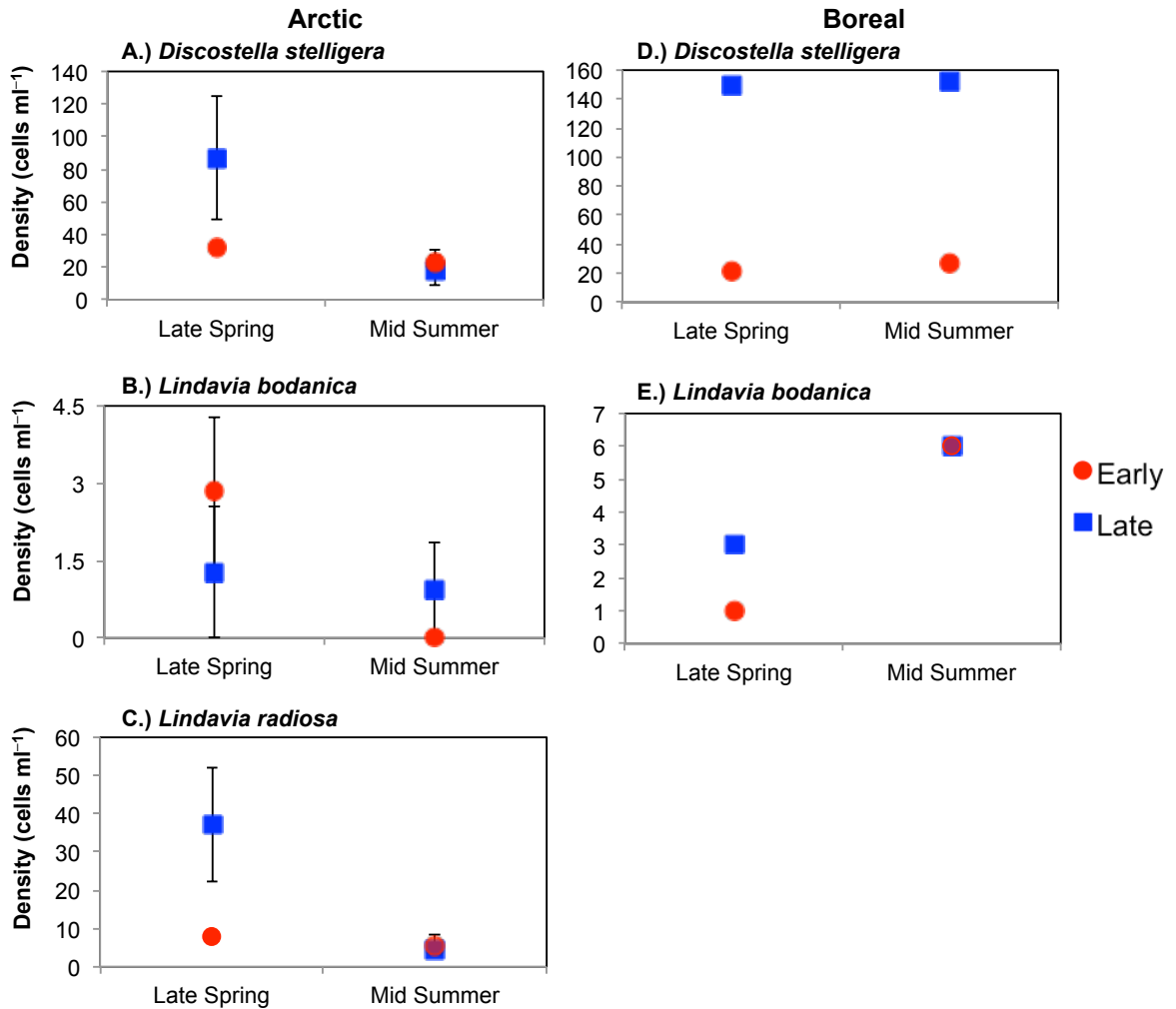


Figure 5.5. Comparison of diatom species in Arctic and boreal lakes. Comparisons are of (A) *Discostella stelligera*; (B) *Lindavia bodanica*; and (C) *Lindavia radiosa* in Arctic lakes and (D) *Discostella stelligera* and (E) *Lindavia bodanica* in a boreal lake for early and late ice-out years. Phytoplankton collection occurred at the time of sampling for all lake metrics for spring and summer and early and late ice-out years. Responses of the three Arctic lakes are averaged (mean \pm standard error) on each date. Purple points indicate overlapping results for early and late ice-out years.

5.4.1.2. Comparison of summer response across early and late ice-out years

Water temperature at 2 m was 1.8 °C higher in the early ice-out year compared to the late ice-out year (2013), the opposite of spring conditions (Figure 5.4). The deeper mixing depths and greater water clarity in the early ice-out year were sustained from spring, with epilimnion thickness 1.3 m greater and Secchi depth 2 m deeper in the early ice-out year compared to the late ice-out year (Figure 5.4). Stability was 14 J m⁻² higher in the early ice-out year compared to the late ice-out year; the opposite of spring conditions (Figure 5.4).

Biogeochemical metrics were variable in the summer season between early and late ice-out years. DIN and TP responded the same as during spring conditions. DIN was 9 µg N L⁻¹ lower and TP was 6 µg P L⁻¹ greater in the early ice-out year compared to the late ice-out year and DIN:TP was 0.9 (indicating N limitation) in the early ice-out year compared to 8.8 (indicating P limitation) in the late ice-out year (Figure 5.4). DOC concentration was higher in the early ice-out year by 1.3 mg L⁻¹ and SUVA₂₅₄ was higher by 1.5 mg C L⁻¹m⁻¹ during early ice-out compared to late ice-out (Figure 5.4).

For algal biomass, average integrated chlorophyll *a* was 0.3 µg L⁻¹ lower in the early ice-out year compared to late ice-out, the same as during spring conditions (Figure 5.4). Diatom cell densities of the three centric species were similar between early and late ice-out years in summer, demonstrating a different response from spring conditions (Figure 5.5).

5.4.2. Boreal region

In Jordan Pond, ice-out occurred 41 days earlier in the early ice-out year, on 19 March 2012 compared to the late ice-out year in which ice-out occurred on 29 April 2015. Air temperature differences between the two years were largest in February and

March and the largest precipitation differences occurred in May. In the early ice-out year, air temperatures were 9.3 °C higher in February and 6.2 °C higher in March compared to the late ice-out year (Figure 5.6). In January and from April to May, air temperature was 1.9 °C higher and ranged from 1.5 °C to 2.3 °C higher in the early ice-out year in comparison to the late ice-out year (Figure 5.6). Precipitation in April and May was 25 mm and 116 mm higher in the early ice-out year compared to the late ice-out year (Figure 5.6). In January and March, precipitation was similar during both early and late ice-out years and in February, June and July, precipitation was slightly lower in the early ice-out year compared to the late ice-out year (Figure 5.6).

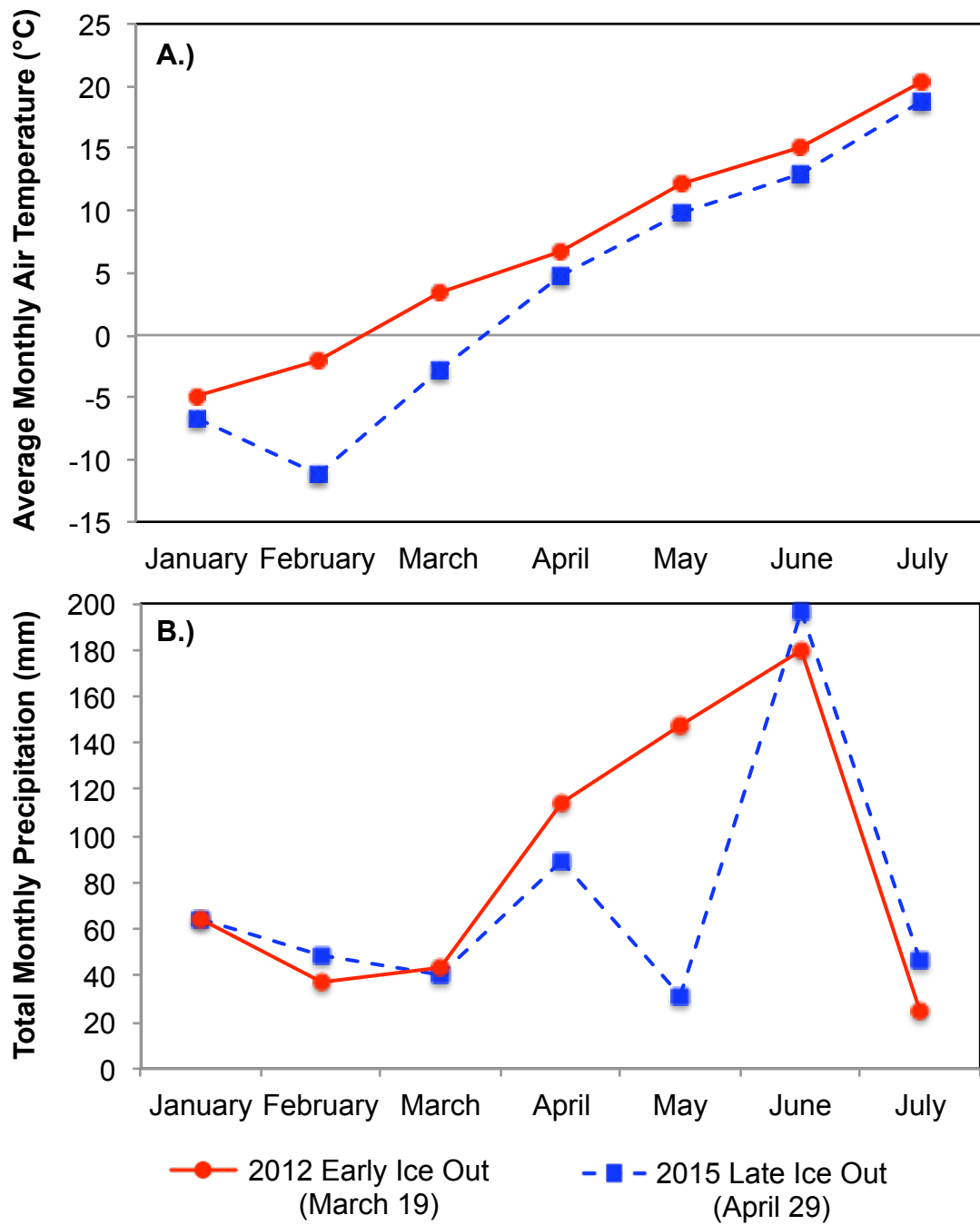


Figure 5.6. Boreal (A) average monthly air temperature in °C and (B) total monthly precipitation in mm for early and late ice-out years.

5.4.2.1. Comparison of spring response across early and late ice-out years

Physical parameters of Jordan Pond varied between early and late ice-out years in spring. Water temperature at 2 m was 0.5 °C higher in the early ice-out year compared to the late ice-out year (Figure 5.7). In the early ice-out year, mixing depths were shallower and water clarity was greater. Epilimnion thickness was 2 m shallower and Secchi depth was 5.9 m deeper in the early ice-out year compared to the late ice-out year (Figure 5.7). Water column stability was 51 J m⁻² higher in the early ice-out year compared to the late ice-out year (Figure 5.7). The onset of stratification in the 2012 early ice-out year was on 18 May and on 20 May during the 2015 late ice-out year.

Biogeochemical metrics were variable in the spring between the two years. DIN concentration was higher by 15 µg N L⁻¹ and TP concentration was the same (2 µg P L⁻¹) in the early ice-out year compared to the late ice-out year and DIN:TP was 11 (indicating P limitation) in the early ice-out year compared to 3.5 (also P limitation) in the late ice-out year (Figure 5.7). DOC concentrations were equal for early and late ice-out (1.7 mg L⁻¹) and SUVA₂₅₄ was higher by 0.2 mg C L⁻¹ m⁻¹ for early ice-out compared to late ice-out (Figure 5.7).

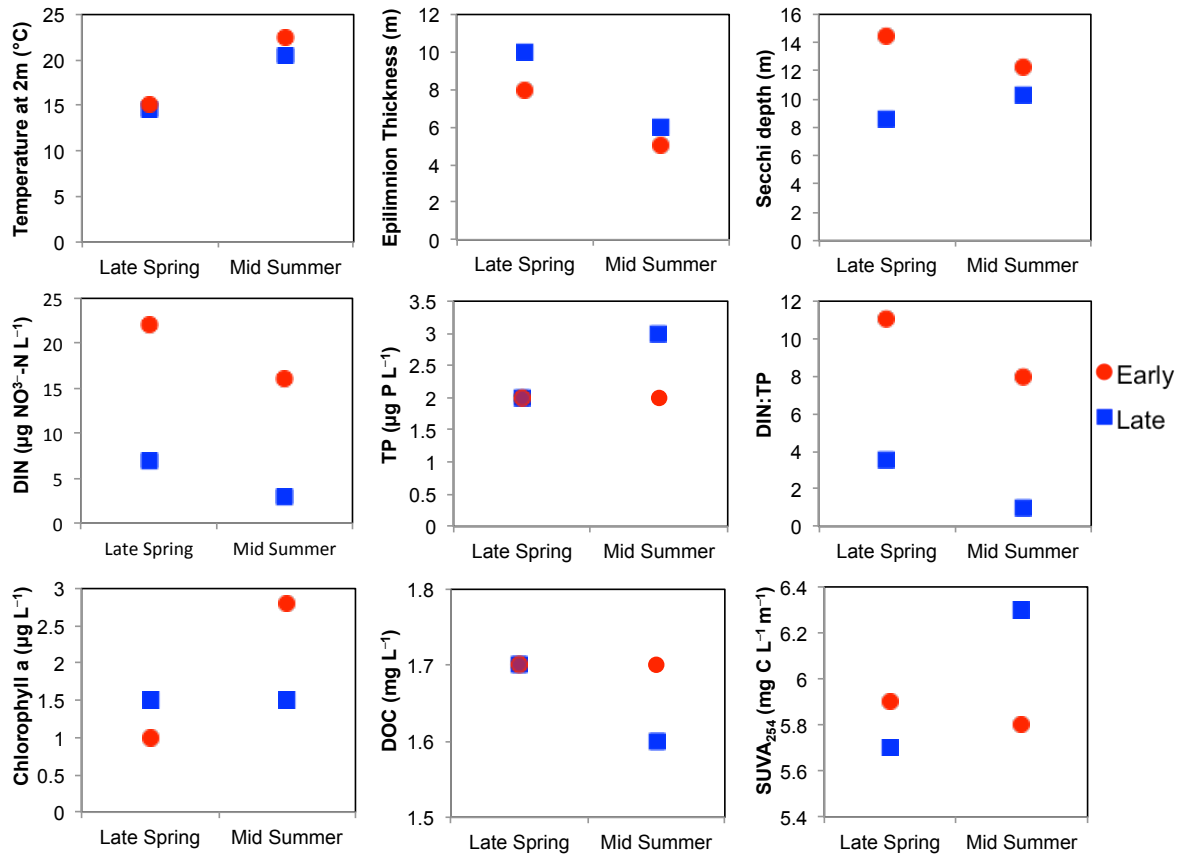


Figure 5.7. Comparison of lake metrics for early and late ice-out conditions during the spring and summer in the boreal lake. Responses represent one sampling for each of the time periods. For the 2012 early ice-out year, spring sampling occurred on 11 June and summer sampling was conducted on 12 July. For the 2015 late ice-out year, spring sampling occurred on 11 June and summer sampling was conducted on 10 July. Purple points indicate overlapping results for early and late ice-out years.

Algal biomass was similar in early and late ice-out years during the spring. The average integrated chlorophyll *a* concentration was $1.0 \mu\text{g L}^{-1}$ in the early ice-out year compared to $1.5 \mu\text{g L}^{-1}$ in the late ice-out year (Figure 5.7). Diatom cell densities in spring of the two centric species present, *D. stelligera* and *L. bodanica*, were both lower in the early ice-out compared to late ice-out year, however the magnitude of response of the two species varied. *D. stelligera* was seven times lower in the early ice-out year ($129 \text{ cells mL}^{-1}$) compared to late ice-out. *L. bodanica* was 2 cells mL^{-1} or three times lower in the early ice-out year compared to the late ice-out year (Figure 5.5).

5.4.2.2. Comparison of summer across early and late ice-out years

In summer, conditions of physical lake metrics were sustained from spring. In the early ice-out year, mixing depths remained shallower and water clarity was greater. Epilimnion thickness was 1 m shallower and Secchi depth was 2 m deeper in the early ice-out year compared to the late ice-out year (Figure 5.7). Stability in summer was 227 J m^{-2} higher in the early ice-out year compared to the late ice-out year (Figure 5.7).

Biogeochemical metrics varied in response between early and late ice-out years and also with season. DIN, TP and DIN:TP were similar across seasons. DIN was $13 \mu\text{g N L}^{-1}$ higher and TP was $1 \mu\text{g P L}^{-1}$ lower in the early ice-out year compared to the late ice-out year and DIN:TP was 8 (indicating P limitation) in the early ice-out year compared to 1 (indicating N limitation) in the late ice-out year (Figure 5.7). DOC quantity and quality differed across seasons during early and late ice-out years. DOC concentration was 0.1 mg L^{-1} higher and SUVA was lower by $0.5 \text{ mg C L}^{-1}\text{m}^{-1}$ for early ice-out compared to late ice-out (Figure 5.7).

Patterns in algal biomass switched from spring to summer during the early and late ice-out years. In contrast to spring, integrated summer chlorophyll *a* concentration

was $1.3 \mu\text{g L}^{-1}$ higher in the early ice-out year compared to late ice-out (Figure 5.7). Cell density patterns of *D. stelligera* were sustained across seasons and were six times lower in the early ice-out year (by $125 \text{ cells mL}^{-1}$) compared to late ice-out. Summer cell densities of *L. bodanica* were equal when comparing early and late ice-out years with concentrations of $6.6 \text{ cells mL}^{-1}$ (Figure 5.5). Overall seasonal patterns of *D. stelligera* and *L. bodanica* suggest that the spring and summer measurements were representative of seasonal patterns. Figure 8 demonstrates similar changes in the two phytoplankton species throughout the spring and summer seasons. *D. stelligera* and *L. bodanica* had lower cell densities during the early ice-out compared to the late ice-out year from May to mid June. *D. stelligera* remained lower from mid June to mid July while *L. bodanica* became more similar between early and late ice-out years. *D. stelligera* were consistently lower throughout the spring and summer seasons in the early ice-out year compared to the late ice-out year, differences throughout the season ranged from 88 to $148 \text{ cells mL}^{-1}$ (Figure 5.8). *L. bodanica* were consistently lower from early May to mid June with differences ranging from 0.5 to $4.4 \text{ cells mL}^{-1}$, slightly higher in early July by $0.96 \text{ cells mL}^{-1}$ and lower by $0.37 \text{ cells mL}^{-1}$ in mid July during the late ice-out year compared to the early ice-out year (Figure 5.8).

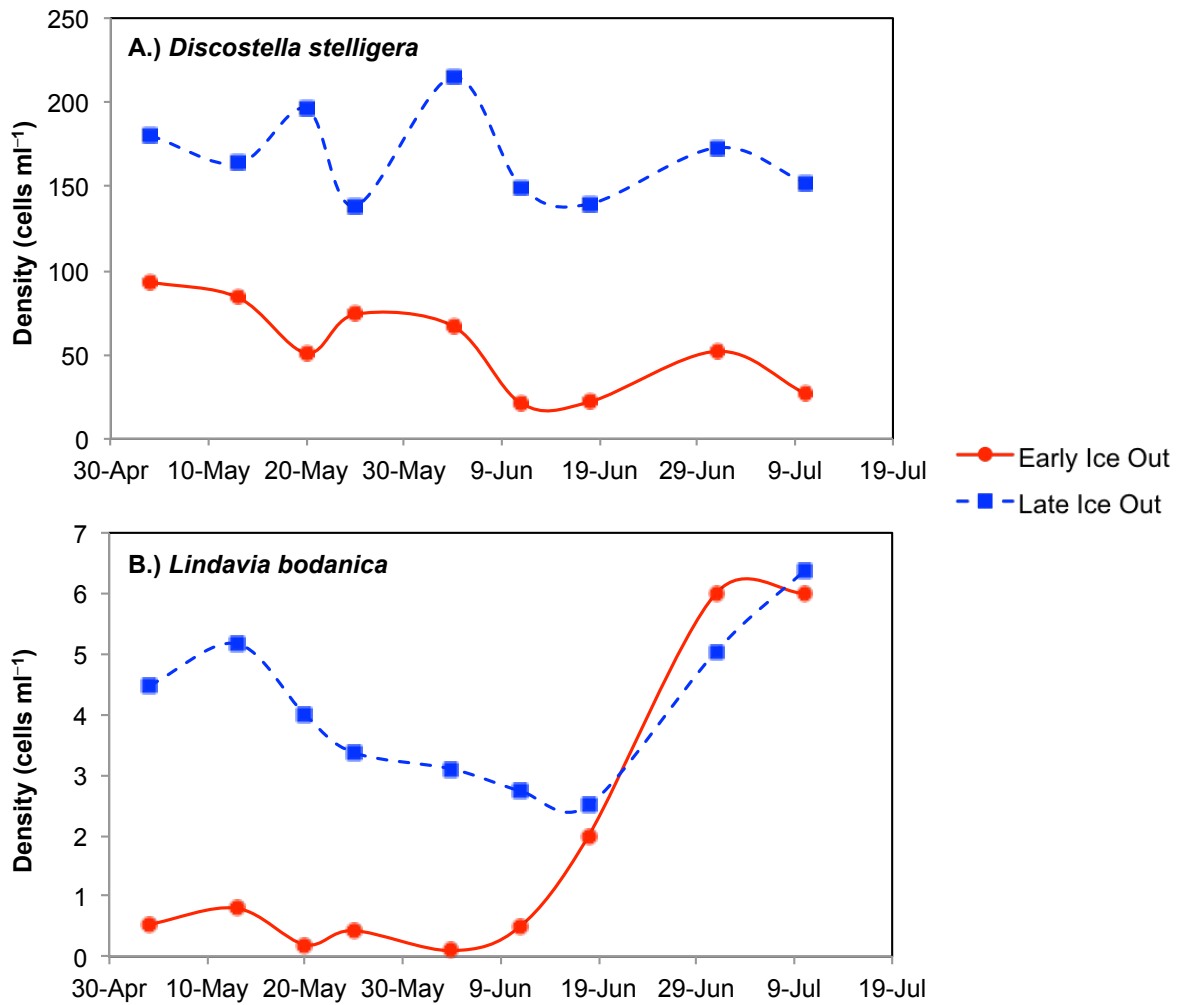


Figure 5.8. Seasonal comparison of (A) *Discostella stelligera* and (B) *Lindavia bodanica* in the boreal lake. Comparisons are from May to mid-July during early and late ice-out years.

5.5. Discussion

Our results reveal differences in the response of certain lake metrics in Arctic and boreal regions between early and late ice-out years. During early compared to late ice-out years, Arctic lakes had deeper mixing depths while the boreal lake had a shallower mixing depth. This supports an influence of the timing of ice-out on the length of spring turnover as well as the strength and stability of stratification but with differing effects between the two regions. Nutrient concentrations and inferred limitation patterns also differed across years and regions, though the effects of other factors that determine nutrient loading to lakes (precipitation, permafrost thaw) likely played a stronger role in driving these patterns than the timing of ice-out. Biological responses in the two years across the two regions also differed, with no differences in algal biomass in the Arctic lakes in relation to ice-out and variable effects over seasons in the boreal lake. The cell densities of key *Cyclotella sensu lato* taxa that respond to thermal structure also varied across the years and regions. Collectively, our results indicate that the timing of ice-out is one important driver among many that influence the physical, chemical and biological responses of lake ecosystems to climate, and that the effects of ice-out timing differ between the two regions.

Stratification patterns differed between ice-out years and regions, likely owing to how the timing of ice-out relates to solar insolation patterns. Ice-out occurs between May and June in Arctic lakes, when solar insolation is near its peak (Kirk 1994; Figure 5.9) and air temperatures are higher, relative to the year, thus Arctic lakes stratify quickly after ice-out. The length of spring turnover is generally short but important for the timing, depth and stability of stratification (Prowse et al. 2006). The rapid warming of surface layers in the late ice-out year, when ice off occurred only four days before the annual

peak insolation, likely led to the observed shallower stratification depths across Arctic lakes. In contrast, ice-out occurs between March and May in boreal lakes, when solar insolation is lower relative to peak insolation (Kirk 1994; Figure 5.9), leading to longer spring turnover periods with extended homothermal mixing of the water column compared to that in Arctic lakes. In the boreal lake, earlier ice-out led to a longer period of spring turnover compared to late ice-out, as the date of the onset of stratification in Jordan Pond for both years was similar. Shallower mixing depths during the early ice-out year correspond with stronger stability, stronger stratification and warmer water temperature at 2 m, similar to observations from King et al. (1999). Compared to the Arctic lakes, the effects of ice-out on the depth and stability of stratification were not as large in the boreal lake, even though the length of the spring turnover period in the boreal lake was 39 days longer. This finding is supported by other work that suggests the timing of the onset of stratification is not directly linked to ice-out timing (Weyhenmeyer et al. 1999; Arvola et al. 2009).

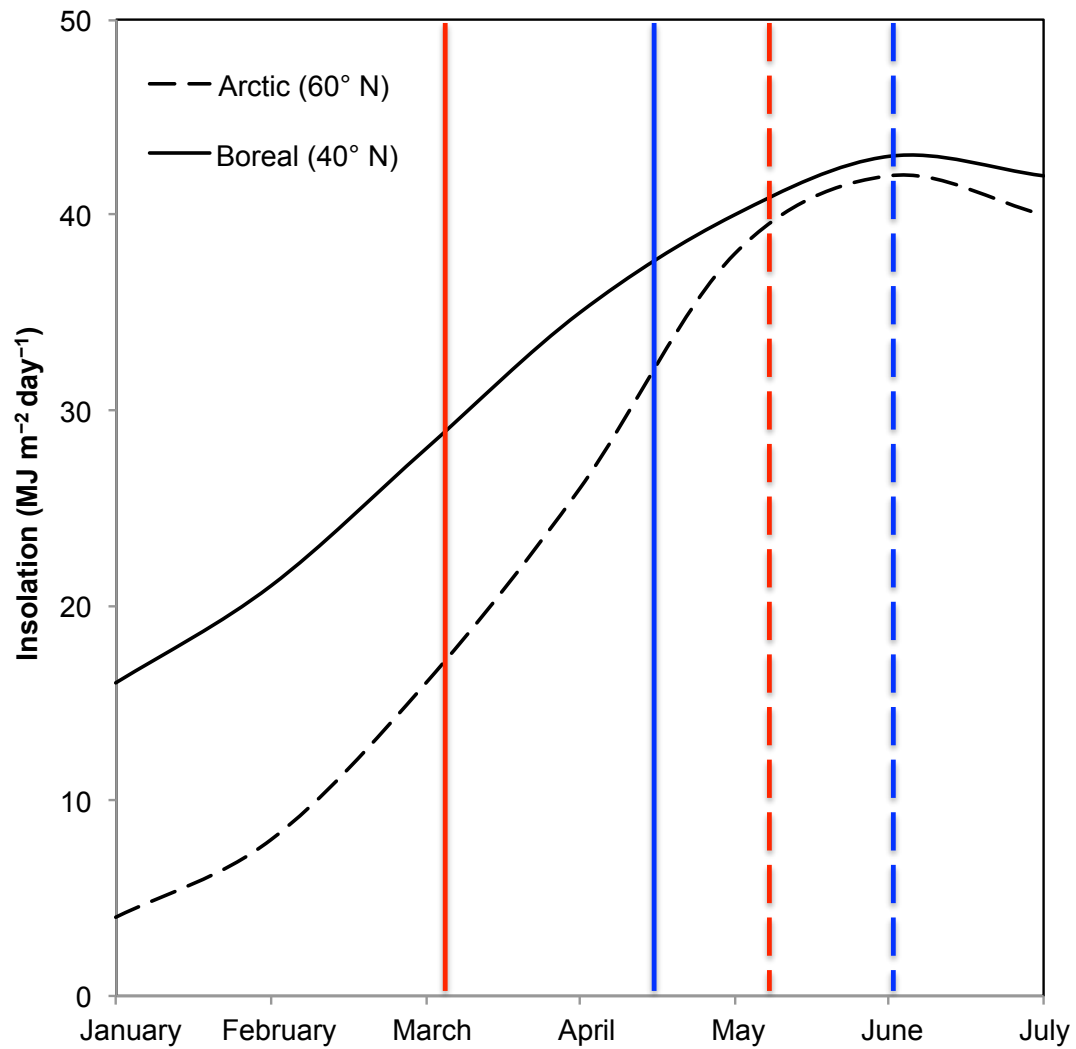


Figure 5.9. Change in daily solar insolation from January through July for 60° N (representative of the Arctic region) and 40° N (representative of the boreal region). Vertical dashed lines indicate early (red) and late (blue) ice-out dates for the Arctic region and vertical solid lines indicate early (red) and late (blue) ice-out dates for the boreal region. Late ice-out is averaged between the 2013 and 2015 ice-out years. Data are plotted from Buffo et al. (1972).

Precipitation amounts were greater in the Arctic and boreal regions during the spring months in the early ice-out years, likely contributing to increased lake water nutrient concentrations. In the early ice-out years, the Arctic region had higher precipitation in May and June and the boreal region had higher precipitation from March through May. Spring precipitation in the Arctic region falls predominantly as snow, including the high precipitation in May during the early ice-out year, which was 82% snow. In the boreal region, precipitation mostly falls as snow from January through March and falls as mostly rain for the remaining spring and summer months. The increased precipitation in May during the early ice-out year fell as rain. Precipitation is a strong driver of increased nutrient inputs to lakes (Jeppesen et al. 2011; Fulton et al. 2015) and has important effects on terrestrial-aquatic linkages. In both Arctic and boreal lakes, nutrient concentrations and ratios in lakes are affected by alterations in terrestrial export related to climate influences on weathering, precipitation and runoff (Bergström and Jansson 2006; Rip et al. 2007). A key variable further influencing terrestrial-aquatic linkages and consequently nutrient limitation patterns in the Arctic, is permafrost thawing. Permafrost thawing is accelerating the delivery of P to many Arctic lakes (Hobbie et al. 1999; Frey and McClelland et al. 2009), in part owing to mobilization of P stored in thawing permafrost as well as to changes in groundwater flow paths. Patterns in nutrient concentrations across years in our study differed regionally. In Arctic lakes, DIN concentrations were lower and TP concentrations were higher during the early ice-out year compared to the late ice-out year. In contrast, DIN concentrations in the boreal lake were higher in the early ice-out year and TP concentrations were the same during the two years. These differences in nutrient concentrations led to varying spring nutrient limitation patterns across the regions. Arctic lakes were N and P co-limited in the early

ice-out year and P limited in the late ice-out year, while the boreal lake was P limited during both early and late ice-out years. Overall, climate differences between the ice-out years likely drove changes in terrestrial-aquatic linkages that dominated the different lake nutrient conditions, independent of direct effects of ice-out.

While precipitation and permafrost thaw are primary drivers of nutrients in lakes, internal processes related to changes in thermal structure can also influence nutrient availability (Jeppesen et al. 2005; Wilhelm and Adrian 2008). Ice-out occurs closer to peak solar insolation in the Arctic lakes, likely contributing to short, perhaps incomplete, turnover periods and rapid stratification with late ice-out, with reduced entrainment of P into the photic zone. In contrast, regardless of ice-out timing, the boreal lake has a longer period of spring turnover than Arctic lakes, leading to complete turnover. These differences, in addition to changes in precipitation and permafrost, may influence nutrient cycling and nutrient availability within the lakes. Changes in the depth of the mixed surface layer, or epilimnion, can also alter nutrient cycling (DeStasio et al. 1996; Wilhelm and Adrian 2008); however, our results do not provide direct links between nutrient availability and thermal structure or the timing of ice-out. In our study, more precipitation occurred during the early ice-out period, after ice-out and before stratification, which may have influenced DIN and TP concentrations due to runoff. It is possible that precipitation, temperature and epilimnion thickness all contributed to varying DIN concentrations and N:P ratios across all lakes, but direct links between nutrients and the timing of ice-out remain unclear. With continued changes in climate, the relationships between nutrient availability and length of spring turnover and lake thermal structure warrant further study.

Secchi depth was deeper during the early ice-out year in all lakes, while DOC concentrations and SUVA₂₅₄ were variable in the Arctic and boreal regions. In the Arctic lake, DOC concentrations and SUVA₂₅₄ were higher in the early ice-out year compared to the late ice-out year and in the boreal lake, DOC concentrations and SUVA₂₅₄ showed little change between ice-out years. DOC strongly influences transparency in lakes and, similar to nutrients, is altered by many factors in addition to ice-out. In the Arctic region, these factors may include precipitation and permafrost thaw and the deepening of soil active layers (Frey et al. 2007; Tank et al. 2012), as well as photodegradation (De Senerpont Domis et al. 2013), which may increase with earlier ice-out. Cory et al. (2014) found changes in DOC may be driven by photochemical oxidation of organic carbon and that sunlight may control the fate of DOC in Arctic surface waters. Our results are inconsistent with photodegradation as a primary mechanism controlling DOC, as DOC concentrations and SUVA₂₅₄ were higher during the early ice-out year. Higher DOC and SUVA₂₅₄ in the early ice-out year suggest that precipitation and permafrost thaw are likely important drivers in explaining our results. Precipitation was higher in May and June during the early ice-out year, which could increase inputs from terrestrial-aquatic linkages. It is important to note that the Arctic lakes in this study have low color DOC (Saros et al. 2016), therefore deep Secchi depths may be accompanied by high DOC concentrations. In the boreal region, DOC is usually dominated by allochthonous material and lake water DOC concentrations often increase with precipitation (Parker et al. 2008). Similar DOC and SUVA₂₅₄ values in early and late ice-out years do not provide evidence to support links between DOC and ice-out, nor do we have enough evidence to elucidate mechanisms in links between similar DOC and deeper Secchi depth in the early ice-out year based on our results. Based on our evidence, differences in climate have strong

controls on changes in DOC, which are likely key contributors to the differences observed in this study, rather than direct effects from ice-out.

Algal biomass varied little between early and late ice-out years in both the Arctic lakes and the boreal lake, with algal biomass generally being slightly lower in the early ice-out years compared to the late ice-out years. An exception to this finding occurred during the summer season in the boreal lake, in which algal biomass was higher in the early ice-out year. This result contrasts with other work that suggests increases in algal biomass due to warming (Persson 1992; Jeppesen 2003; Hansson 2012) and earlier ice-out regimes (De Senerpont Domis et al. 2013); however, Kraemer et al. (2017) found that there is not a direct relationship between warming and algal biomass. Instead, lake surface temperature and trophic state are important in determining algal biomass, thus nutrients and light may be key contributors in algal biomass response and not only lake warming or direct ice-out effects.

The responses of key diatom taxa that are often indicators of thermal structure conditions varied across the two regions. In the Arctic lakes, differences in thermal stratification depths across ice-out years affected cell densities of key diatom taxa in the spring. Cell densities of *D. stelligera* and *L. radiosa* were lower during the early ice-out year, with deeper mixing depths, compared to the late ice-out year. *Discostella stelligera* is more abundant in lakes with shallower mixing depths (Saros et al. 2016), and *L. radiosa* is more abundant under high light conditions typical of shallower mixing depths (Malik and Saros 2016). In contrast, cell densities of *L. bodanica* were higher during the early ice-out year with deeper mixing depths; this taxon has a deeper mixing depth optimum than other *Cyclotella* taxa (Bergstöm 2010). Patterns for these species in Arctic lakes indicated a strong relationship with mixing depth, resulting in differences in cell

densities across differing ice-out years. In contrast, links between these taxa and thermal structure were less clear in the boreal lake. *Discostella stelligera* was more abundant in the late ice-out year, which had deeper mixing depths; this pattern was sustained over the entire open-water season. The same pattern was observed for *L. bodanica*, even though mixing depths showed only small differences across the two ice-out years. Boeff et al. (2016) also found that *D. stelligera* was more abundant in some Maine lakes in late ice-out years, in contrast to the early ice-out patterns found in some other areas (Rühland et al. 2008; Wiltse et al. 2016). The effects of the complex interactions between light and nutrients on *Cyclotella* taxa are well known and reviewed by Saros and Anderson (2015), and are likely behind the weaker links between thermal structure and taxon responses in this boreal lake compared to those observed in Arctic lakes.

Identifying seasonal effects throughout the open water season provides important insights into the differences between lake responses in Arctic and boreal regions. In Arctic lakes, with the exception of temperature at 2 m, spring and summer response of lake metrics (Figure 5.4) are sustained between the seasons from the early ice-out year to both the 2013 and 2015 late ice-out years. The biggest difference between spring and summer was a decrease in overall cell densities of phytoplankton (Figure 5.5). The change in water temperature across the Arctic lakes was likely due to differences between the different late ice-out years used in this study. The boreal lake had larger differences in the lake metric values between spring and summer and a switch in algal biomass and SUVA₂₅₄ concentrations between the early and late ice-out years (Figure 5.7). The use of two different late ice-out years for the Arctic region make comparisons between spring and summer difficult, however the variation in lake metric values, cell densities of phytoplankton and changes in lake characteristics between the Arctic and boreal regions

are likely due to climate conditions at ice-out, which include differences in solar insolation, precipitation and temperature, as well as differences in the timing of stratification relative to ice-out between the two regions. Further investigation of how changes to lake variables are sustained throughout the season relative to ice-out and climate factors could provide important insights about drivers of change in phytoplankton community structure.

Our research provides evidence that lake responses in Arctic and boreal regions differ between early and late ice-out years. However, it is ultimately a combination of climate factors, importantly solar insolation, air temperature, precipitation, and, in the Arctic, permafrost thaw, that are key drivers of the observed responses. Key findings of this study include regional differences in mixing depths and the relationships between length of spring turnover and the strength and stability of stratification. These differences, in concert with climate factors, have further implications for nutrient and light availability and subsequent effects on phytoplankton community structure and biomass. Future work that explicitly examines the pathways and links between the physical and biological effects would strengthen the understanding of how the timing of ice-out influences the biological properties within lakes. Regional differences within the Northern Hemisphere can elicit contrasting lake responses, which will be altered with future climate changes, thus underscoring the importance of this research.

CHAPTER 6

CONCLUSION

The goal of this research was to demonstrate how precipitation events affect DOC in aquatic ecosystems and identify potential losses associated with changes in water quality. This research investigated changes in both DOC quantity and DOC quality metrics. There were consistent patterns of change in DOC response from individual storm events and there were consistencies in the response of DOC quality metrics across lakes during different times of year. This research evaluated a method to link changes in DOC from precipitation events to WTP estimates. The responses in DOC quantity and quality were dependent on lake and watershed specific characteristics. Changes in DOC were correlated to changes in water clarity and secondarily WTP, which was also dependent on lake and watershed specific characteristics. Response of DOC to precipitation events during different times of year and response of Arctic and boreal lakes during early and late ice-out years were mediated by climate factors.

In chapter 2, precipitation events contributed to short-term abrupt changes in DOC quantity and quality. Three key patterns of DOC response emerged from the results of this study, an immediate spike, a sustained increase, and no changes in DOC concentration in response to precipitation events. The same patterns were revealed in the response of $SUVA_{254}$, a^*_{320} , and a^*_{380} with an increase in the variability in the response in lakes where DOC concentrations did not change. A key driver of observed changes in DOC concentration and quality metrics was residence time, and WA:LA likely also contributed to lake response. Research from this chapter helps to preemptively alter management strategies to ensure high water quality for drinking water resources.

In chapter 3, changes in DOC concentration and SUVA₂₅₄ corresponded to changes in Secchi depth and secondarily to WTP from improved water quality. WTP was highest in lakes with Secchi depths that ranged from 2 to 4 m and lowest in lakes with Secchi depths that were deeper than 6 m. WTP values also correlated to the maximum depth of each lake, residence time, percent wetland coverage, and DOC and SUVA₂₅₄. This research demonstrates a cost effective and simple method to link changing DOC from precipitation events with losses due to changes in water quality, while acknowledging that improved methodology and connection between the ecological data and economic models would substantially improve WTP estimates.

In chapter 4, DOC quality metrics responded differently to an early summer storm compared to an autumn storm, while response of mean DOC concentration was similar across lakes. Storm response was mediated by a combination of lake and watershed characteristics and seasonal changes in climate such as solar radiation and antecedent weather conditions were also likely important factors affecting DOC response. The balance of the response of DOC quality metrics during the early summer storm suggest photobleaching was the dominant process, whereas the balance of the response of DOC quality metrics during the autumn storm suggest increased allochthonous inputs and bacterial processing were the dominant processes contributing to change. Findings from this chapter reveal important variation in DOC quality metrics during different times of year, which could assist with improved monitoring or management of aquatic resources.

In chapter 5, the response of certain lake metrics in Arctic and boreal regions differed between early and late ice-out years. A combination of climate factors, including solar insolation, air temperature, precipitation, and, in the Arctic, permafrost thaw, were key drivers of observed lake responses. Mixing depths and the relationships between

length of spring turnover and the strength and stability of stratification differed between regions. These differences have important implications for nutrients and light availability for phytoplankton communities. The results indicate that the timing of ice-out is one important driver among many that influence the physical, chemical and biological responses of lake ecosystems to climate.

Broadly, this research provides insight into patterns of response that persist due to particular climate changes to help further research and understanding. Collectively, chapters 2 and 3 help to establish a baseline for implications to water treatment systems and for establishing adaptive management strategies from precipitation events. Chapter 4 provides important contributions to evaluation of DOC quality metrics in addition to research on DOC concentration and attempts to link response to precipitation events to seasonal variation. Chapter 5 addresses regional differences climate factors which affect lake response that vary between early and late ice-out years. These findings that ultimately result from changes in climate have important implications for lake structure and function and can help to inform adaptive strategies and management decisions to protect these important resources.

Future research is important as precipitation events are predicted to continue to increase in frequency and intensity, particularly in the autumn months. Therefore, increased variability in lakewater DOC metrics may be expected in the future. This research serves as a starting point for establishing adaptive management strategies. Continued evaluation of the response of DOC quality metrics (in addition to DOC concentration) from precipitation events may help to further the research on identifying pre-cursors to DBP's. Additional monitoring of DOC concentration and quality from storm events with further analysis of how this may vary during different times of year

could improve the effectiveness of management plans and potentially reduce costs. In particular, better integrated ecological and economic models could significantly improve adaptation and management strategies as ecological models often do not contain certain data relevant to the economic models. Establishing a better understanding of these relationships between physical and chemical changes in aquatic ecosystems is important, and future research connecting physical and biological properties of lakes is also important for maintaining aquatic ecosystem structure and function. Identifying changes in phytoplankton community response may reveal insights into taste and odor problems for drinking water utilities or identify key changes that could affect the base of the food web.

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**APPENDIX A: MAINE DRINKING WATER PRECIPITATION, NUTRIENT,
AND CHLOROPHYLL INFORMATION**

Methods

Precipitation amounts before and during sampling periods

Table A.1. Total storm precipitation amounts are indicated in bold for each of the six study lakes. Total precipitation amounts for the 14 days before the pre sampling period, between P1 and P2, and between P2 and P3 sampling periods with maximum daily precipitation amounts indicated in parentheses. All precipitation amounts are in mm.

	Young Lake (Northern Maine Regional at Presque Isle Station)	Floods Pond Nokomis Pond (Bangor International Airport Station)	Chases Pond (Pease International Tradeport Station)	Jordan Pond (ACAD-MH)	Sebago Lake (Portland International Airport Station)
Storm 1 (9/30/15)	45.2	139.2	71.6	84.1	149.9
14 days prior – Pre	3.1 (3.1)	0	0.3 (0.3)	0	0.3 (0.3)
P1 – P2	0	0	0	0	0
P2 – P3	17.0 (6.9)	23.4 (11.9)	13.0 (9.4)	27.4 (17.8)	17.5 (10.9)
Storm 2 (10/28/15)	29.7	38.4	45.0	62.5	40.1
14 days prior – Pre	17.5 (4.3)	15.2 (5.8)	5.1 (2.5)	15.5 (5.8)	8.9 (4.6)
P1 – P2	3.0 (3.0)	1.5 (1.5)	0.3 (0.3)	1.3 (1.3)	0.8 (0.8)
P2 – P3	14.5 (4.8)	8.6 (6.6)	26.2 (23.4)	10.9 (8.9)	7.9 (5.8)
Storm 3 (11/19/15)	25.4	23.1	27.2	23.1	37.3
14 days prior – Pre	11.4 (4.8)	8.4 (6.6)	26.2 (23.4)	10.9 (8.9)	7.9 (5.8)
P1 – P2	0	9.7 (9.7)	9.1 (7.9)	28.4 (24.9)	8.6 (5.3)
Storm 4 (6/5/16)	15.2	18.0	31.2	25.9	61.7
14 days prior – Pre	20.8 (5.6)	5.1 (3.3)	8.6 (6.4)	2.3 (1.0)	7.9 (2.8)
P1 – P2	7.1 (3.6)	23.4 (15.2)	0	7.4 (4.1)	5.1 (4.6)
P2 – P3	76.5 (26.7)	54.6 (13.5)	29.2 (12.4)	46.0 (12.4)	47.0 (23.1)
Storm 5 (19/21/16)	30.7	33.5	80.5	30.2	108.5
14 days prior – Pre	23.9 (13.7)	1.8 (1.5)	32.8 (32.5)	44.2 (26.9)	21.6 (20.6)
P1 – P2	2.3 (2.3)	0	0	0	0

Analysis of nutrients and chlorophyll *a*

Water collected in the opaque 1-L acid washed bottle for each of the storm sample collections was analyzed for total phosphorus (TP), total nitrogen (TN), nitrate (NO_3^-) and ammonium (NH_4^+). Unfiltered TP and TN samples were analyzed using persulfate digestion followed by the ascorbic acid method (TP) on a Varian Cary UV-VIS spectrophotometer, and the cadmium reduction method (TN) on a Lachat QuickChem 8500 flow injection analyzer (APHA, 2000). TP samples had a limit of quantification of $1 \mu\text{g L}^{-1}$ and TN had a limit of quantification of $5 \mu\text{g L}^{-1}$. NO_3^- and NH_4^+ samples were filtered through 25 mm Whatman GF/F filters pre-rinsed with deionized water. Samples were quantified using the cadmium reduction method (NO_3^-) and the phenate method (NH_4^+) on a Lachat QuickChem 8500 flow-injection analyzer (APHA, 2000) with quantification limits of $2 \mu\text{g L}^{-1}$.

Algal biomass was measured as chlorophyll *a* for all pre and post samples. Samples were filtered through 25mm Whatman GF/F filters, wrapped in aluminum foil and frozen until analysis. All chlorophyll samples were filtered within 2 weeks of filtration and processed using standard methods (APHA, 2000). Filters were ground and chlorophyll was extracted in 90% acetone overnight. Samples were centrifuged and chlorophyll *a* concentrations were analyzed by spectrophotometry on a Varian Cary-50 Ultraviolet Visible spectrophotometer.

Changes in mean nutrient (TP, TN, NO_3^- , NH_4^+) and chlorophyll *a* concentrations across all five storms were assessed using ANOVA and Tukey's post hoc test. All Post samples were compared to Pre samples, P1 was compared to P2 and to P3, and P2 was compared to P3 for each of the 6 lakes separately to identify changes before and after the storm events.

Results

Comparison of lake surface water and intake samples

Chlorophyll *a* concentrations were similar, with the biggest differences in Jordan Pond and Nokomis Pond (Table S1). Nutrient concentrations varied the most between lake surface water and intake with NO_3^- , NH_4^+ , and TN having the same or slightly higher concentrations in water collected from the intake in all but two samples (Floods Pond, NH_4^+ and Nokomis Pond, TN; Table S1). TP was slightly higher in lake surface water in all lakes except Chases Pond (Table S1).

Table A.2. Comparison of samples taken from lake surface water and the intake on the same or similar days.

Lake	Date	Source	Chl. <i>a</i> ($\mu\text{g L}^{-1}$)	NO_3^- ($\mu\text{g L}^{-1}$)	NH_4^+ ($\mu\text{g L}^{-1}$)	TN ($\mu\text{g L}^{-1}$)	TP ($\mu\text{g L}^{-1}$)
Floods	8/11/15	lake	1.4	5	19	117	2
	8/11/15	intake	1.9	5	11	119	1
Jordan	10/7/15	lake	2.6	2	5	45	1
	10/6/15	intake	1.7	5	5	56	1
	10/22/15	lake	1.8	4	13	43	3
	10/20/15	intake	1.5	6	16	53	1
Chases	10/20/15	lake	2.3	5	4	85	1
	10/20/15	intake	2.1	5	8	94	2
Nokomis	11/3/15	lake	3.8	11	15	239	5
	11/3/15	intake	2.4	15	19	222	5

Response of nutrients and algal biomass

In general, nutrient concentrations varied across the 6 study lakes and there were no patterns similar to those that emerged from DOC concentration and quality metrics, with the exception of TN and TP in Young Lake. Within each lake, mean nutrient concentrations from the 5 storms were not significantly different between Pre, P1, P2,

and P3 sampling periods ($p > 0.05$; Figure S1). While not significant, TN and TP in Young Lake did spike from Pre to P1 and decrease thereafter ($p > 0.05$; Figure S1).

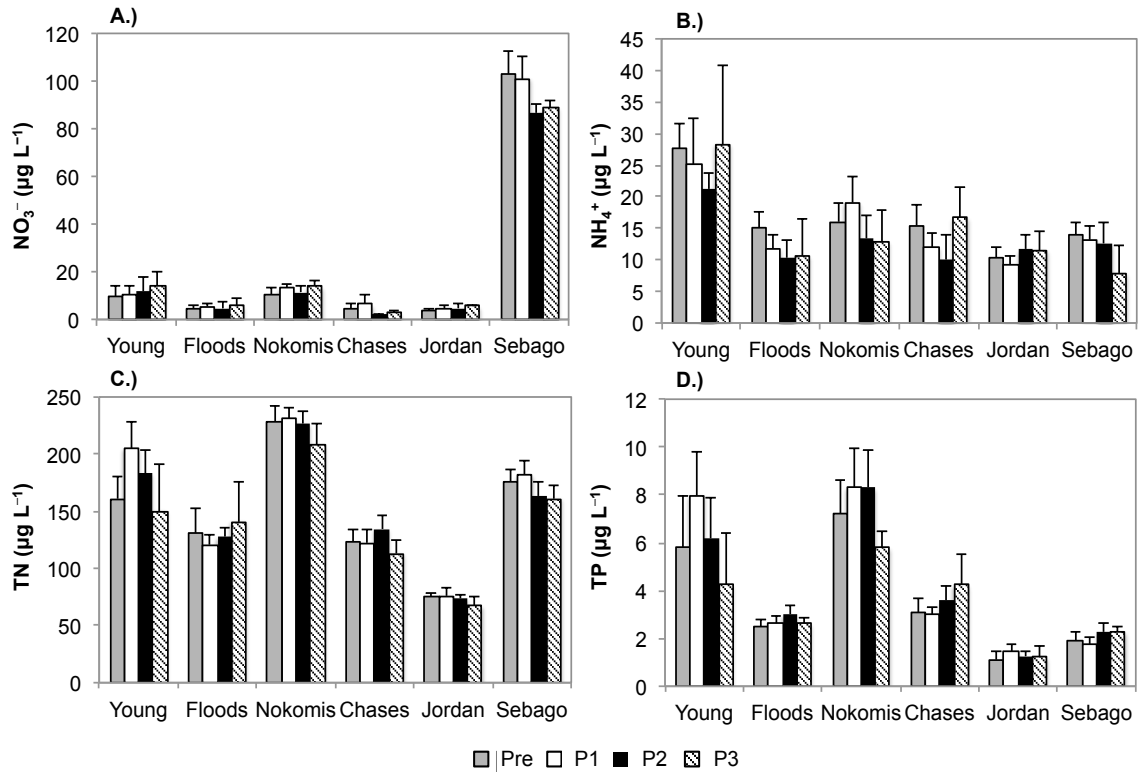


Figure A.1. Mean concentrations (\pm standard error) from the 5 storms for the 6 study lakes of A.) nitrate, B.) ammonium, C.) total nitrogen, and D.) total phosphorus.

Across all 6 study lakes, chlorophyll *a* concentrations ranged from 0.9 to 3.7 $\mu\text{g L}^{-1}$. There were no significant relationships between the mean chlorophyll *a* concentrations and the sampling period. In general, chlorophyll *a* concentrations increased from the Pre to the P1 sampling and increased again to the P2 sampling, followed by a decline in the P3 sampling (Figure S2). The increase in percent change from Pre to P2 in all lakes, ranged from 20% in Sebago Lake to 60% in Young Lake and Nokomis Pond (Figure S2).

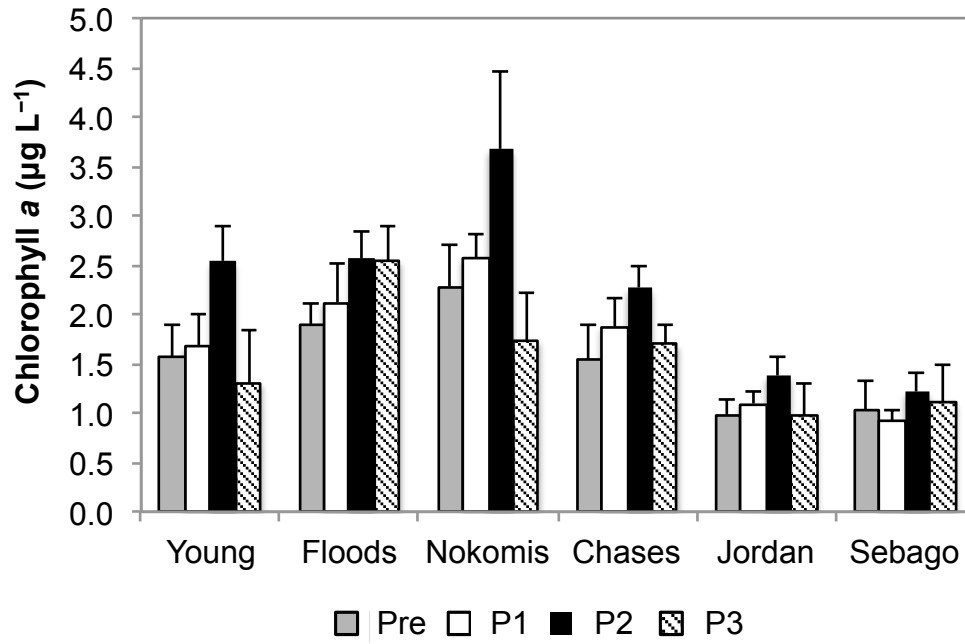


Figure A.2. Mean chlorophyll *a* concentrations (\pm standard error) from the 5 storms across the 6 study lakes.

**APPENDIX B: ACADIA DOC PERCENT CHANGE DATA FROM AN EARLY
SUMMER AND AUTUMN STORM EVENT**

Table B.1. Initial pre-storm values and percent change for P1 and P2 samplings. Values are for [DOC], SUV_{A254} , $S_{275-295}$, $E_2:E_3$, and $S_{275-295}$, for each of the 6 study lakes and mean initial values and mean percent change (\pm standard error) of the 6 study lakes for P1 and P2 samplings for the same DOC metrics. White columns indicate the Early Summer storm and gray columns indicate the Autumn storm.

Lake	[DOC] (mg L ⁻¹)		SUV_{A254} (L mg-C ⁻¹ m ⁻¹)		a^{*320} (L mg-C ⁻¹ m ⁻¹)		a^{*380} (L mg-C ⁻¹ m ⁻¹)		$E_2:E_3$		$S_{275-295}$ (mm ⁻¹)	
	Early Summer	Autumn	Early Summer	Autumn	Early Summer	Autumn	Early Summer	Autumn	Early Summer	Autumn	Early Summer	Autumn
Jordan												
Initial value	1.8	1.6	5.04	3.95	1.50	0.99	0.63	0.27	7.1	9.7	0.022	0.027
P1 (% change)	1.8	1.4	-10.0	-0.1	-11.9	2.2	-21.4	5.8	-5.3	6.0	6.3	-2.3
P2 (% change)	1.8	0.6	-10.0	1.4	-14.4	6.1	-33.9	23.3	18.5	-8.4	8.1	-2.6
Bubble												
Initial value	1.7	1.6	5.00	3.10	1.48	0.75	0.53	0.23	7.1	9.6	0.022	0.026
P1 (% change)	5.7	2.3	-7.0	12.7	-7.3	26.6	-16.2	16.4	4.9	-4.2	1.8	-5.7
P2 (% change)	0.4	5.7	-4.4	11.6	-4.9	32.0	-15.1	36.6	15.4	-18.3	3.6	-9.1
Eagle												
Initial value	1.9	1.7	4.13	3.05	1.13	0.70	0.42	0.18	7.8	11.3	0.024	0.028
P1 (% change)	14.0	-3.4	-10.3	7.0	-8.6	5.9	-11.2	62.8	-2.3	-0.7	1.7	-0.4
P2 (% change)	-3.6	-5.7	-3.6	9.4	-7.4	12.9	-18.6	35.9	12.6	-9.9	5.8	-0.4
Echo												
Initial value	2.7	2.3	5.47	4.31	1.68	1.09	0.57	0.36	7.4	9.4	0.022	0.025
P1 (% change)	3.3	-0.4	-4.6	0.0	-3.0	-1.8	8.8	7.6	-9.9	-6.3	0.0	1.1
P2 (% change)	-2.5	-1.4	-3.2	10.2	-6.9	32.1	-11.5	75.3	10.9	-34.4	4.6	-7.9
Long												
Initial value	2.9	2.6	6.27	5.14	2.17	1.55	0.78	0.51	6.3	7.4	0.019	0.022
P1 (% change)	0.7	-0.9	-1.8	1.4	0.1	1.3	-0.7	-3.8	-2.3	6.7	-3.6	-0.9
P2 (% change)	-2.7	-3.2	-2.4	3.5	-3.8	3.2	-7.0	-0.6	5.1	3.4	3.1	-0.5
Seal Cove												
Initial value	4.3	3.8	6.26	4.52	2.16	1.29	0.73	0.41	6.5	8.2	0.019	0.023
P1 (% change)	-4.8	-7.0	0.7	10.8	-0.5	21.2	-1.6	53.1	2.4	-19.5	1.6	-6.1
P2 (% change)	-6.1	-5.6	0.8	3.4	-2.0	2.4	-4.0	4.0	6.0	1.4	2.6	1.3
Mean												
Initial value	2.6±0.4	2.3±0.3	5.36±0.3	4.01±0.3	1.69±0.2	1.06±0.1	0.61±0.05	0.33±0.05	7.0±0.2	9.3±0.5	0.021±0	0.025±0
P1 (% change)	3.4±2.5	-1.3±1.4	-5.5±1.8	5.3±2.3	-5.2±2.0	9.2±4.8	-7.1±4.6	23.7±11.2	-2.1±2.2	-3.0±3.9	1.3±1.3	-2.4±1.2
P2 (% change)	-2.1±1.1	-1.6±1.8	-3.8±1.4	6.6±1.8	-6.6±1.8	14.8±5.7	-15.0±4.3	29.1±11.2	11.4±2.1	-11.0±5.7	4.7±0.8	-3.0±1.8

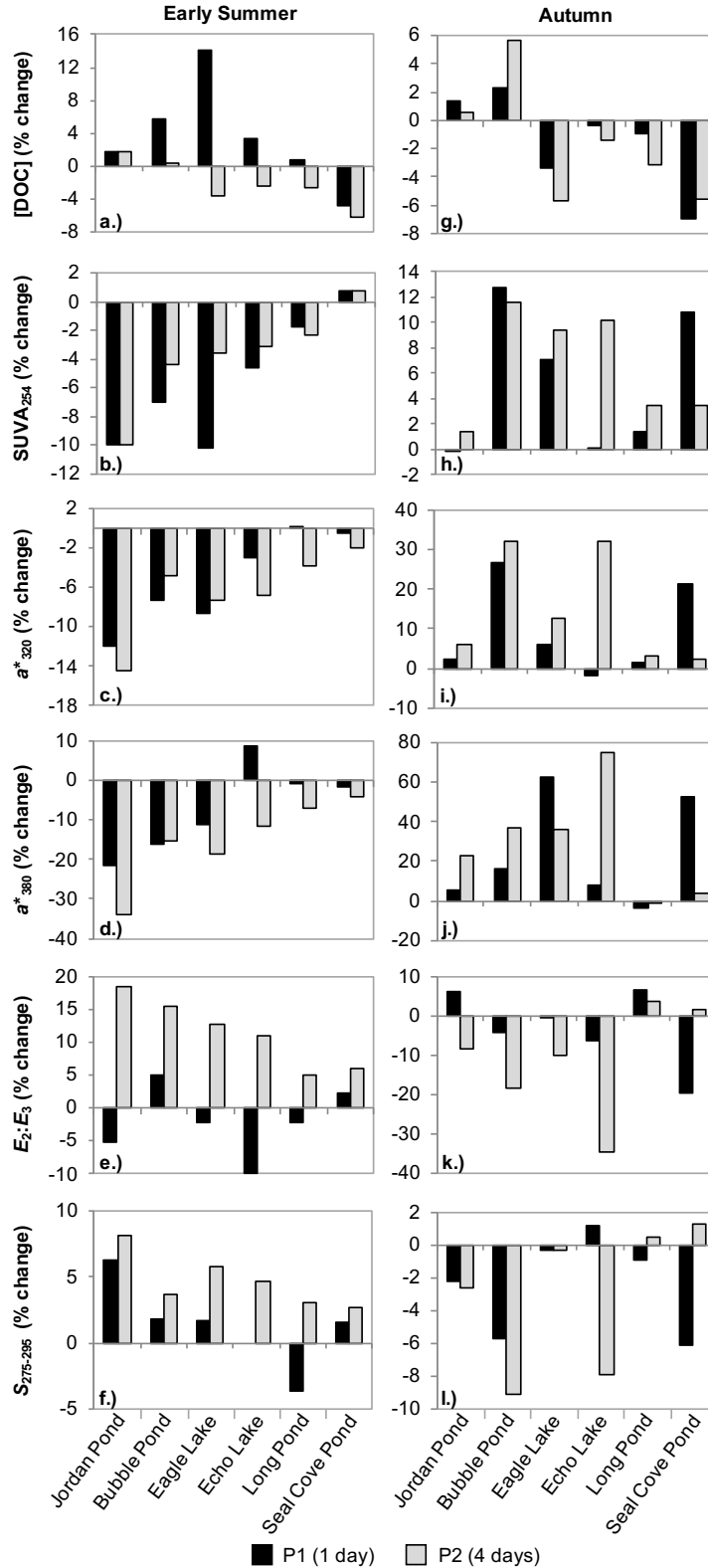


Figure B.1. Percent change for each lake in response to the Early Summer storm (a-f) and to the Autumn storm (g-l). Responses are for [DOC] (a,g), SUVA₂₅₄ (b,h), *a**₃₂₀ (c,i), *a**₃₈₀ (d,j), *E*₂:*E*₃ (e,k), and *S*₂₇₅₋₂₉₅ (f,l) during P1 and P2 samplings indicated by black and gray respectively.

APPENDIX C: ICE OUT DATES FOR ARCTIC AND BOREAL LAKES

C.1. Ice-out dates from 2010 to 2016 for the Arctic lakes and the boreal lake. Ice-out is defined as the first date that the lake is completely ice-free.

Year	Arctic (Greenland)	Boreal (Jordan Pond)
2010	24 May	22 March
2011	14 June	16 April
2012	3 June	19 March
2013	9 June	4 April
2014	13 June	14 April
2015	17 June	29 April
2016	17 May	17 March

BIOGRAPHY OF THE AUTHOR

Kathryn Warner was born in Danvers, Massachusetts on March 29, 1984. She grew up in Hamilton, Massachusetts and later moved to Gloucester, Massachusetts. She graduated from Gould Academy in Bethel, Maine in 2002. She then attended Hobart and William Smith Colleges in Geneva, NY and graduated with a Bachelor of Arts Degree in Environmental Science in 2006. After graduation Kathryn worked as an Environmental Scientist at EBI Consulting in Massachusetts for the next two years. Kathryn then spent her winters in Colorado where she coached ski racing and worked with the local high school, and spent her summers as an educator at Maritime Gloucester teaching students in Kindergarten through 12th grade. She received her Master of Science Degree from the University of Maine in 2013, after which she decided to pursue a PhD. Kathryn is a candidate for the Doctor of Philosophy degree in Ecology and Environmental Science from the University of Maine in May 2019.