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Physical and Chemical Response of Small, North Temperate Lakes to Recovery From Acidification and Climate Change

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PHYSICAL AND CHEMICAL RESPONSE OF SMALL, NORTH TEMPERATE LAKES TO RECOVERY FROM ACIDIFICATION AND CLIMATE CHANGE

By

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A THESIS

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Thesis Advisor: Dr. Sarah J. Nelson

An Abstract of the Thesis Presented
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As the rate of sulfate (SO_4^{2-}) deposition continues to decline and climate is trending towards warmer and wetter conditions, the biogeochemical and physical response of small, north temperate lakes is variable. In this study, we observed long-term chemical trends combined with seasonal water temperature patterns in the context of climate change and recovery from acidification in two remote lake populations in Maine: 29 high elevation lakes and eight low elevation lakes. Small, temperate lakes are the most abundant type of lake, making them a widely representative study sample to consider.

Maine's high elevation lakes (>600m) could potentially provide unique insight into the response of surface water chemistry to declining acidic deposition and interannual climate variability. The geochemical response in 29 lakes was analyzed during 30 years of change in sulfate (SO_4^{2-}) deposition and climate. All 29 lakes exhibited positive trends in DOC from 1986-2015, and 19 of 29 lakes had statistically significant increases in DOC throughout the study period. These results illustrate a region-wide change from low DOC lakes (<5 mg/L) to moderate DOC lakes (5-30 mg/L). Increasing DOC trends for these high elevation lakes were more consistent than for lower elevation lakes in the northeastern US. A linear mixed effects model demonstrated that lakewater SO_4^{2-} and climate variables describe

most of the variability in DOC concentrations (r^2 = 0.78), and the strongest predictor of DOC concentration was an inverse relationship with SO_4^{2-}. Due to SO_4^{2-} concentrations trending towards pre-acidification levels and projections of a warmer, wetter, and more variable climate, there is uncertainty for the future trajectory of DOC trends in surface waters. Long-term monitoring of Maine's high elevation lakes is critical to understand the recovery and response in surface water chemistry to a changing chemical and physical environment in the decades ahead.

DOC trends in lower elevation lakes were more variable. We hypothesize this is attributed to different levels of SO_4^{2-} deposition and availability of DOC in these watersheds, which varied in size and landscape character. We used high frequency temperature arrays to observe stratification dynamics during summer 2017. We hypothesized that lakes with higher DOC concentrations will exhibit a larger ratio of hypolimnion volume: total lake volume, and therefore have a larger volume of cold-water refugium that is less likely to warm or disappear over the course of a summer stratification period. We found the strongest predictors of percent change of hypolimnion volume ratio (HVR) were both the interaction of DOC concentration and maximum lake depth and just DOC concentration. This suggests that deeper and darker lakes are more likely to maintain larger hypolimnia and cold-water refugia over the course of summer stratification than shallower lakes. Schmidt stability quantifies the strength of stratification, and a significant, inverse relationship between mean Schmidt stability and percent change in (HVR) suggests that morphometry matters; lakes with greater stratification stability and simple basin morphometry are more likely to maintain larger hypolimnia throughout the course of summer stratification

The disproportionately large contribution of small lakes to the global carbon cycle deem them an ideal system to observe and quantify changing DOC dynamics. Disentangling the effects of climate, acidification, and individual lake characteristics on small, north temperature lakes is critical to

understanding the biogeochemical response of freshwater to a changing physical and chemical environment in the decades to come.

DEDICATION

This is dedicated to my family: Janelle, Kevin, John, Joe, and Tracy Lane. I appreciate your endless support, gracious acts of kindness, willingness to tackle any challenge, and spontaneous approach to life. I feel incredibly lucky to have both deep roots and encouragement to spread wings.

ACKNOWLEDGEMENTS

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understanding high elevation lake systems, and we appreciate her dedication to researching and advocating for Maine's high elevation lakes. I would like to thank Mike SanClements and the lab at INSTAAR for graciously analyzing DOC quality data. I would like to thank Kaizad Patel for teaching me DOC quality lab work and being available to answer any other questions that I had. I would like to thank non-committee manuscript co-authors, Kristin Strock, Amanda Klemmer, Bill McDowell, and Mike SanClements for their dedication to assisting and revising my work and valuable scientific insight. Ken Johnson was a great help in the field and graciously available to help portage canoes into remote Maine lakes. Finally, I would like to thank the 30 years of field technicians that came before me, and all of the field volunteers who came out to help me continue long-term lake monitoring.

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CHAPTER 1

ACIDIFICATION AND CLIMATE LINKAGES TO INCREASED DISSOLVED ORGANIC CARBON IN HIGH ELEVATION LAKES

Introduction

Recovery from acidification and climate change have been linked to increased dissolved organic carbon (DOC) concentrations in lakes across the US and northern Europe (Monteith et al., 2007; SanClements, Oelsner, Mcknight, Stoddard, & Nelson, 2012; Strock et al., 2016). DOC, a weak acid that can lower pH, is a critical component of biological, physical, and chemical processes within lakes (Brown, Nelson, & Saros, 2017; Driscoll, Lehtinen, & Sullivan, 1994; Williamson, Morris, Pace, & Olson, 1999). Temporal increases in DOC have been referred to as “brownification”, which describes the yellow-brown color caused by dissolved humic matter from terrestrial and wetland areas that is characteristic of DOC-rich lakes. Darker water absorbs more ultraviolet radiation, which can alter physical, biological, and metabolic processes in lakes (Strock et al., 2016; Williamson et al., 2015, 1999). Due to a lack of baseline DOC data prior to SO_4^{2-} induced acidification, it is unclear whether increased DOC concentrations in recent decades represent a return to a natural, high-DOC state that was present prior to anthropogenic atmospheric deposition, or a new state responding to a range of anthropogenic disturbances, like acidic deposition and climate change (Erlandsson et al., 2011). A myriad of complex biological, physical, chemical, and climatic interactions complicates the study of DOC variability.

Disentangling the drivers of recent increases in freshwater DOC concentrations is difficult due to the confounding signals of climate change and recovery from acidification [*Strang and Aherne*, 2015]. Several studies indicate that increasing DOC concentrations across the US and northern Europe are driven by recovery from acidification (Evans, Chapman, Clark, Monteith, & Cresser, 2006; Monteith et al., 2007; Sanclements et al., 2018; SanClements et al., 2012; Sawicka et al., 2017). The underlying mechanism for an inverse relationship between SO_4^{2-} and DOC in freshwaters is decreasing acidity,

attributed to declining SO_4^{2-}, and the subsequently diminishing ionic strength of soil solutions, which promotes DOC mobilization (Ekström et al., 2011; Evans et al., 2006; Hruška, Krám, Mcdowell, & Oulehle, 2009; SanClements et al., 2012). Changes in land-use and land management practices have also been linked to increasing DOC concentrations in the northern hemisphere (Kritzberg, 2017; Meyer-Jacob, Tolu, Bigler, Yang, & Bindler, 2015). In addition to the chemistry of precipitation influencing delivery of DOC to lakes, there is growing evidence in the literature that points to climatic factors contributing to DOC variability (Clark, Chapman, Adamson, & Lane, 2005; Couture, Houle, & Gagnon, 2012; de Wit et al., 2016; Zhang et al., 2010).

Terrestrial ecosystem research and laboratory experiments demonstrate that microbial activity can control DOC production; for example, DOC release from litter was positively correlated with temperature [*Gödde et al.*, 1996]. Rates of biological activity and thus DOC production in soil are also influenced by wetting and drying cycles and antecedent moisture (Christ & David, 1996; Dawson et al., 2008; Naden et al., 2010; Pagano, Bida, & Kenny, 2014). *Raymond and Saiers* [2010] described temperature and antecedent conditions as drivers for the relationship between DOC concentration, flux, and event discharge and found the largest DOC fluxes occurred during warmer, wet periods following a dry period. The delivery of terrestrial DOC from soils to surface waters can increase through hydrologic flushing during large precipitation events, which leads to enhanced flow through shallow flow paths (Boyer, Hornberger, Bencala, & McKnight, 1996; de Wit et al., 2016; Jennings et al., 2012; McDowell & Likens, 1988). Thus, increases in DOC concentrations in lakes have been pronounced in extreme wet and warm years across several freshwater ecosystems (Clark et al., 2005; Couture et al., 2012; de Wit et al., 2016; Strock et al., 2016; Zhang et al., 2010).

The impacts of atmospheric deposition and climate variability in North America’s high elevation lakes have been studied in Colorado, California, and British Columbia, Canada, where high elevation, headwater catchments are more likely to have sparse vegetation and represent true alpine ecosystems

(Parker, Vinebrooke, & Schindler, 2008; Sadro & Melack, 2012; Strang & Aherne, 2015; Turk & Adams, 1983). There are few studies in the northeastern US that isolate high elevation lakes for biogeochemical research. The most notable efforts have been in New York's Adirondack Mountains, but these lakes are also influenced by high nitrogen deposition (Aleksic et al., 2009; Civerolo, Roy, Stoddard, & Sistla, 2011; Driscoll, Driscoll, Fakhraei, & Civerolo, 2016). Maine's high elevation lakes and their response to air pollution and climate change provide a unique opportunity to study the effects of environmental change on an acid-sensitive lake region. Because they receive more precipitation than lower elevation lakes and are characterized by steep slopes, shallow, acidic soils with lower base saturation, and non-calcareous bedrock that is relatively resistant to weathering, high elevation lakes in the northeastern US are more vulnerable to SO_4^{2-} deposition and acidification than lowland lakes (Baumann, 2011; Norton, Brakke, Kahl, & Haines, 1989). Studying the DOC trends in these lakes will contribute to understanding the recovery from acidification and climate variability on vegetated, sub-

alpine headwater catchments (Figure 1.1.).

Figure 1.1. Photograph of Tumbledown Pond. This photo illustrates the exposed bedrock, high relief, and sub-alpine vegetation that are characteristic of High Elevation Lake Monitoring sites in Maine.

The purpose of this study was to explore the DOC response in lakes from the Maine High Elevation Lake Monitoring (HELM) project in the context of multi-decadal trends in acid deposition and climate. In contrast to most other long-term lake monitoring sites in New England, HELM lakes are distant from roads, road salt applications, homes, agriculture, industry, and motorized boat use. Their remoteness provides reference conditions relatively free from local anthropogenic stressors common in the northeastern US, allowing the study of atmospheric deposition decoupled from significant land-use related changes in the catchment. The long-term dataset and the remoteness of the lakes have the potential to provide unique insight into multi-decadal changes in Maine's surface water chemistry.

Materials and Methods

In the late 1980s, in response to acidification of freshwater bodies, the US Environmental Protection Agency (US EPA) created a Long-Term Monitoring (LTM) program to study the effects of congressionally mandated decreases in sulfur dioxide (SO2) and nitrogen oxides (NOx) emissions on northeastern lakes [Kahl et al., 2004]. In 1990, the Clean Air Act Amendments (CAAA) set regulations on industrial emissions of sulfur (S) and nitrogen (N) to further aid in reduction of acidic deposition that affected fresh waters in the region. Demonstrated by continuous monitoring since the 1980s, improved air quality has greatly reduced the acidity of most of Maine's freshwaters toward pre-industrial conditions [Kahl et al., 2004]. The HELM project emerged in 1986 in response to the recognition that Maine had 60 lakes with acid neutralizing capacity (ANC) less than 0 μeq/L (extremely acidic), yet 45 of these were too high and too small to be included in the RLTM (Regional Long-Term Monitoring) program network described by Kahl et al., [2004] or the 1984 US EPA Eastern Lake Survey (ELS) [Kahl and Scott, 1988].

The HELM project sampled all 90 high elevation lakes in Maine in 1986 [Kahl and Scott, 1994]. Minimum elevation for selection of HELM lakes was 600 m above sea level (asl), a function of the number of candidate lakes and the physical geography of Maine, to allow comparison with studies from

New York's Adirondack Mountains [Schofield, 1976; Kahl and Scott, 1988]. As per the initial HELM selection criteria, lake depth was greater than 1 m, minimum lake surface area was 0.4 ha, there were no stream inflows or outflows, and there were no beaver impoundments [Baumann, 2011]. In comparison to the ELS lakes, HELM lakes are smaller and positioned at higher elevations, but the watershed to lake area ratio is similar between the two lake sets [Kahl et al., 1991]. High elevation lakes in Maine are drainage lakes, a characteristic that is shared with 91% of all Maine lakes [Kahl, 1998]. The vegetation is primarily evergreen boreal forest that is dominated by the spruce-fir cover type [Kahl, 1998]. The HELM project has continued after the 1980s under the umbrella of US EPA LTM monitoring, using the same methods, QAPP (Quality Assurance Project Plan), and laboratories as other project components (e.g., Kahl et al. 2004, Strock et al. 2014, 2016; See Text 1: Laboratory Quality Assurance Information)

Chemically, acid deposition influences HELM lakes more than any other lake subset in Maine are different from other subsets of Maine lakes [Kahl, 1998]. Based on 1986 sampling data, HELM lakes are more acidic, have lower ANC, lower Ca^{2+}, Mg^{2+}, Cl^{-}, and higher SO_4^{2-} than ELS lakes [Norton et al., 1989]. Evidence from paleolimnological reconstruction for three of the HELM lakes (Ledge, Tumbledown, and Speck) showed that these lakes were acidified over the last 100 years [Davis et al., 1983]. We used data from the 29 HELM lakes that were sampled most frequently over the thirty-year study period (Figure 1.2.). This subset was chosen to represent many of the lakes with initially low ANC, those with the greatest relief, and to include 10 of the 13 acidic HELM lakes [Baumann, 2011].

To provide a direct comparison of DOC and SO_4^{2-} trends in high elevation and low elevation lakes, we also assessed a set of lower elevation lakes from the Maine RLTM project that have a similar sampling history and protocol to HELM lakes. Of the 16 Maine RLTM lakes, 15 were included in this study; one was omitted because the initial sample was collected in 1997. RLTM lake elevation ranges from 63 - 381 m asl, with a mean elevation of 127 m asl. Median RLTM lake size is 11 ha, which is larger

than the median HELM lake size of 3.3 ha. RLTM lakes are predominantly drainage lakes but include three seepage lakes. Mixed deciduous-coniferous stands dominate the forests; the median percent coniferous forest for RLTM lakes is 39%, compared to 75% in HELM lakes [Homer et al., 2015]. With the exception of one sandstone and limestone lake basin, RLTM lake bedrock geology is Devonian granite [Osberg et al., 1985; Brown et al., 2017].

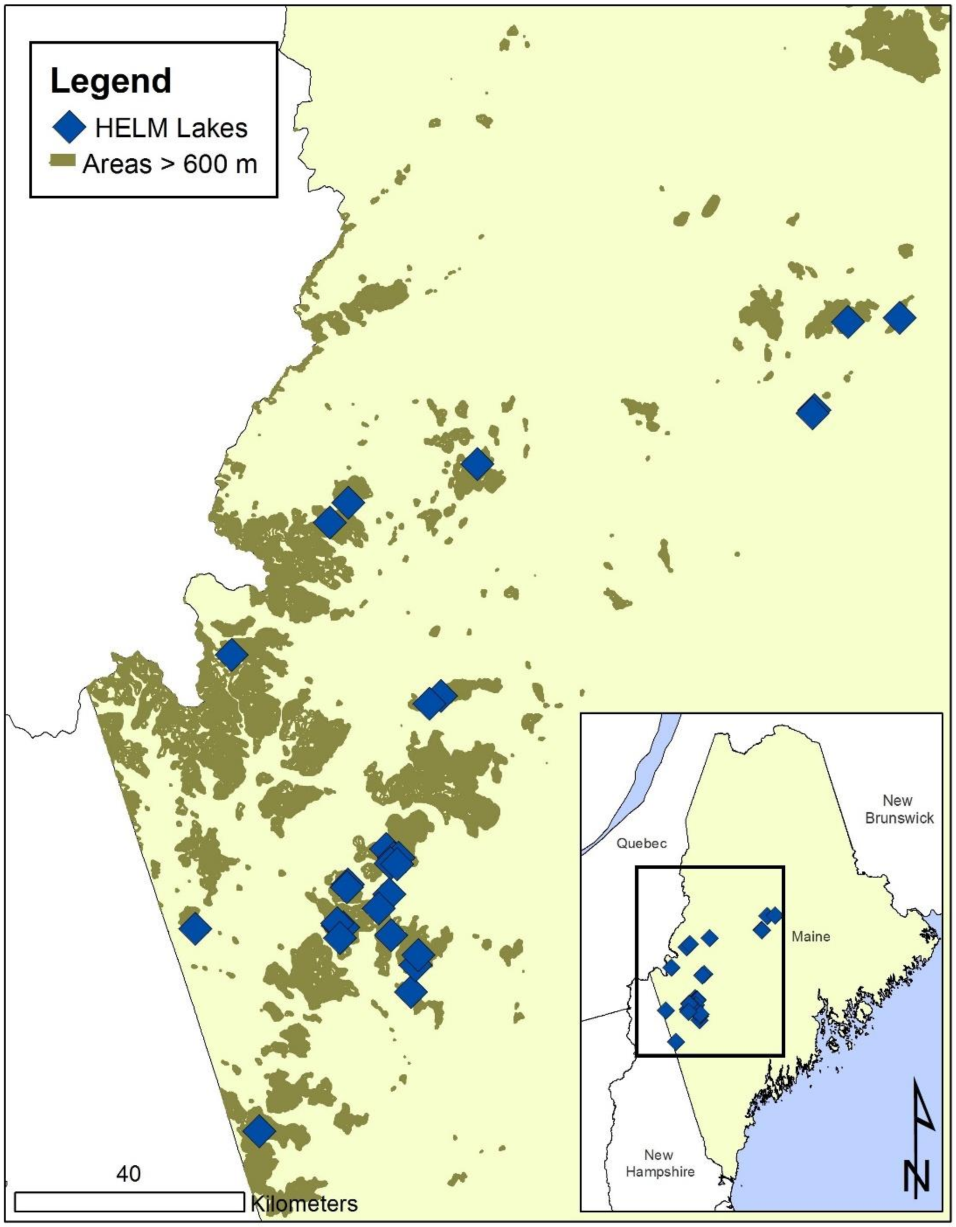

Figure 1.2. Location of 29 High Elevation Lake Monitoring lakes in Maine. Blue squares represent the 29 lakes that have had consistent monitoring and were used in this study. Dark green areas are greater than 600 meters in elevation.

HELM lakes were sampled in both summer and fall (1986, 1987, 1998, 1999, and 2000) and only fall (1997 and 2001 – 2015) to meet standard base flow criteria [Landers et al., 1988; Kahl et al., 2004]. Minimal sampling (fewer than five lakes per year) was done between 1988 and 1996. To account for potential changes in chemistry from summer to fall, we only used fall samples in this analysis. In 1997, HELM lakes were sampled twice, once in October and once in November, and only the October sampling was included in analyses. However, as a separate case study, we explored variation in water chemistry between these two sample periods in 1997. RLTM lakes were sampled in the spring, summer, and fall, and we only included fall sampling in this study for consistency. Due to their remoteness, HELM lakes were routinely accessed by helicopter, with a few exceptions when lakes were visited on foot and sampled by small inflatable raft. All RLTM lakes were sampled from nonmotorized boats. Samples were collected in pre-cleaned HDPE bottles and syringes (for closed-system pH), at ~0.5 m depth. Sampling methodology was consistent with that described in Strock et al., [2014] and Kahl et al., [2004]. Samples were placed on ice and returned to the University of Maine, University of New Hampshire, or Plymouth State University analytical laboratories at the end of each sampling day. Information on laboratory consistency is included in Appendix Text 1: Laboratory Quality Assurance Information**.**

. Lake water samples were analyzed for air-equilibrated and closed-system pH, ANC, SO_4^{2-} and other anions, cations, aluminum (total and organic), conductivity, and DOC. Laboratory methods for all analytes follow standard EPA protocols outlined in Hillman et al., [1986] and summarized by Stoddard et al., [1999]. Geographical Information Systems (ArcGIS 10.1) were used to extract landscape data for each watershed. Each lake's watershed was delineated using the National Hydrography Dataset Plus Version 1 (NHDPlusV1). Quality assurance on lake and watershed boundaries was done by cross checking NHDPlusV1 data with topographic contours and larger watershed delineations (HUC 12) provided by the Maine Office of GIS and Maine Department of Environmental Protection.

Climate in recent decades in New England can be characterized by increases in air temperature, precipitation, and the frequency and intensity of weather extremes (drought, heat waves, heavy precipitation) [Salinger, 2005; Horton et al., 2014; Ning et al., 2015]. Coupled with significantly shorter ice over periods, earlier and accelerated spring melt, and increasing rain/snow ratio, these observed changes have the potential to impact catchment biogeochemistry and aquatic biota [Moore et al., 1997; Hodgkins et al., 2002; Huntington et al., 2004; Hayhoe et al., 2007; Horton et al., 2014; Monahan et al., 2016]. Between 1985 and 2014, annual precipitation in the state of Maine has increased approximately 150 mm, and mean annual air temperature has increased approximately 1.7 ˚C [Fernandez et al., 2015]. Models predict that annual air temperature will increase an additional 1.1 to 1.7 ˚C by 2050 [IPCC, 2007; Fernandez et al., 2015]. The projected increase in air temperature and time between precipitation events also increases the potential for drought [Madsen and Fidgor, 2007]. This paradox can be explained by the concentration of precipitation in large events that are interspersed with dry periods with increased evapotranspiration [IPCC, 2007]. Maine's Climate 1 Northern Division, which is home to the half of the state and includes the high elevation lake region of this study (Figure 1.2.), is predicted to have the greatest increases in temperature and precipitation across the state, coupled with up to 20% decreases in annual precipitation as snow between 2014 and 2054 [Fernandez et al., 2015].

Parameter-elevation regressions on independent slopes model (PRISM) was used to determine monthly rainfall and mean air temperature for the high elevation lake region. PRISM data are generated by statistical modeling between available data stations at a resolution of 4 km and were accessed via Climate Reanalyzer [PRISM, 2004; Climate Reanalyzer, 2016]. Due to severe weather and difficult access, micrometeorological data are sparse at high elevations, so a necessary strength of PRISM is its ability to capture climate variability with elevation using weighted climate-elevation regression functions [Daly et al., 2002; Richardson et al., 2004]. PRISM also accounts for topographic relief and terrain variability by dividing the terrain into topographic facets [Daly et al., 2002]. With PRISM, we could model climate for

the entire region, which allowed us to consider regional watershed responses, and for the 29 individual lake basins, to consider localized climate influences. Monthly and seasonal temperature and precipitation for the HELM region is summarized in Appendix Tables 1 and 2, respectively.

Surface water chemistry data compiled over the 30-year span of the HELM project were combined with regional and individual lake basin weather data and landscape data for statistical analyses. The residuals from model fits were normally distributed and met the assumptions of normality, so the use of simple linear regression was appropriate. A weighted least squares (WLS) approach allowed us to use all years in the study period, even when a small number of lakes were sampled each year, and we weighted each point by the number of lakes sampled. WLS was applied to DOC, SO_4^{2-}, and CV (coefficient of variation) regressions. SO_4^{2-} was log transformed for analysis of SO_4^{2-} time series and regression with DOC (Figure 1.3. and Figure 1.5.) to meet the assumptions of normality. Statistical results are presented using log transformed values; however, Figure 1.3. and Figure 1.5. display raw SO_4^{2-} data for ease of visual interpretation. Linear regression was used to analyze precipitation, air temperature, DOC, and SO_4^{2-} trends over an annual time step. Linear regression was also used with DOC as the dependent variable and SO_4^{2-}, mean annual temperature, and annual precipitation as independent variables. For the climate timeseries, DOC and climate regression plots, and DOC CV analyses, we used the 12 months prior to sampling (November-October) to create an annual mean temperature and total precipitation variable that represented the year prior to our October sampling dates and avoided the inclusion of November and December temperatures that occurred after the majority of HELM sampling.

Linear regression was also used to analyze the relationship between net changes in DOC and SO_4^{2-} in both HELM and the lower elevation, RLTM lakes. To obtain net change values, we subtracted the median of both DOC and SO_4^{2-} values for the first three years of the study period from median values of

both DOC and SO_4^{2-} calculated from the last three years of the study period. Net changes in SO_4^{2-} met the assumptions for normality, so SO_4^{2-} concentrations were not log transformed in this analysis. Due to inconsistent sampling at the beginning of the HELM study period, only values from 1986 are used to represent initial SO_4^{2-} and DOC concentrations in HELM lakes. Speck Pond (MIDAS number 3288; MIDAS is a unique identification number assigned to all ponds and lakes in Maine), was also not included in this analysis because its initial sample in 1986 did not include DOC, and it was not sampled again until 1997. Six RLTM lakes had consistent monitoring during 1986, 1987, and 1988, so initial concentration calculations were calculated from the median of these three years. The remaining nine RLTM lakes were initially sampled in 1993, so DOC and SO_4^{2-} concentrations from 1993, 1994, and 1995 were used to obtain the initial median value. Both lake populations had complete sampling in 2013, 2014, and 2015, so these years were used to calculate the median values for the end of study period. To determine whether using initial median concentration values calculated from both 1986-1988 and 1993-1995 was valid, we compared the difference in DOC and SO_4^{2-} in median concentrations from 1986-1988 to median concentration values from 1993-1995 in the 6 RLTM lakes that had been sampled consistently since 1986. Median SO_4^{2-} concentrations differed on average by 4.0 µeq/L, and median DOC concentrations differed by a maximum of 0.24 mg/L. Because these changes were relatively small, we deemed it reasonable to use medians derived from two different time periods to represent initial concentrations. Additionally, Strock et al., [2014] found that the rates of change for SO_4^{2-} and DOC concentrations were greater in the 2000s than in the 1990s, so we know that the early 1990s was not a period of rapid chemical change.

The CV provides a standardized measure of dispersion of a variable; as used here it is a useful tool to compare the variability in DOC concentrations among years. The CV of surface water DOC concentration within the population of lake study sites was determined for each study year with sufficient data by dividing the standard deviation of DOC of all lakes by the DOC mean of all lakes for a

specific year. This demonstrated the degree of relative variability of DOC concentrations across HELM lakes within a year and allowed comparison of how similarly or differently the set of HELM lakes DOC responded to precipitation or air temperature. A low CV indicates low variability among lake DOC concentrations within a given year. In this analysis, CV was chosen instead of standard deviation because normalization of the standard deviation with respect to the mean allows comparison between years with different mean DOC concentrations. The number of lakes sampled each year varied, but WLS standardized the regression to account for the number of lake samples per year. Four years were not included in the CV analysis because they had five or fewer lake samples per year. Linear regression was used to assess relationships between CV and climate variables. We then ran individual regressions for the relationship between CV and mean temperature for each month of the year prior to sampling.

To analyze the effects of climate and SO_4^{2-} on DOC, we constructed a linear mixed effects model using the "lme4" package in R [Bates et al., 2015]. Seasonal temperature and precipitation for each individual lake and annual SO_4^{2-} concentrations were entered as fixed effects. SO_4^{2-} was log transformed to meet assumptions of normality. One 1987 data point from Moose and Deer Pond (MIDAS number 3548) was removed from this analysis as an outlier. DOC concentrations exceed 2.5 standard deviations above the mean for both mean 1987 DOC concentrations of all lakes and mean Moose and Deer DOC concentration for the whole study period. To compare the strength of dependent variables, all dependent variables were converted to z scores. Individual lakes were entered into the model as the random effect, which controlled for the variability among lakes. Selecting only climate variables and SO_4^{2-} as dependent variables allowed us to quantify the specific effects of climate and acidification on DOC and avoid issues with multicollinearity that arise when including many chemical analytes and landscape characteristics. To obtain p-values for each explanatory variable, we used the "car" package in R to perform a Wald test [Fox and Weisberg, 2011]. Linear relationships were considered significant if p

≤ 0.05. All statistical analyses were conducted using R software 2.12.1 [R Development Core Team, 2011].

Results

In the high elevation lakes region in Maine, air temperature increased an average of 0.04 ˚C per year during the 30-year study period (p = 0.004) (Figure 1.3.a). The highest mean annual temperature recorded was 6.5 ˚C in 2010. Annual mean temperature was lowest in 1992 at 3.7 ˚C. Annual precipitation in the HELM region increased an average of 7 mm per year throughout the study period (p = 0.01) (Figure 1.3.b). Mean annual precipitation for the study period was 1170 mm. In the HELM region, the wettest year of the study period was 2005 (1551 mm precipitation), and the driest year was 2001 (893 mm precipitation). Most precipitation occurred between June and August, except for 2005, when approximately 600 mm (two-thirds of the precipitation received in an average precipitation year), occurred between September and November (SI Table 3).

The mean DOC concentration across all lakes sampled in a year increased significantly (p = 0.0002) at an average rate of 0.12 mg/L per year (Figure 1.3.c). The mean DOC concentration across all lakes for the first three years of the HELM project was 4.3 mg/L and was 6.9 mg/L for the last three years of the study period, a 60% regional increase. Conversely, mean SO_4^{2-} concentration across all lakes sampled in a year decreased significantly at an average rate of -2.1 μeq/L per year (p < 0.001) (Figure 1.3.d). The mean SO_4^{2-} concentration across all lakes for the first three years of the HELM project was 92.8 μeq/L and 38.4 μeq/L for the last three years of the study period, a 59% decline. Individual lake concentrations of DOC throughout the study period ranged from 0.1-15.5 mg/L and the mean (±SD) DOC concentration across all lakes was 6.3±2.9 mg/L. SO_4^{2-} ranged from 21.2-127.0 μeq/L and the mean (±SD) was 57.9±22.1 μeq/L.

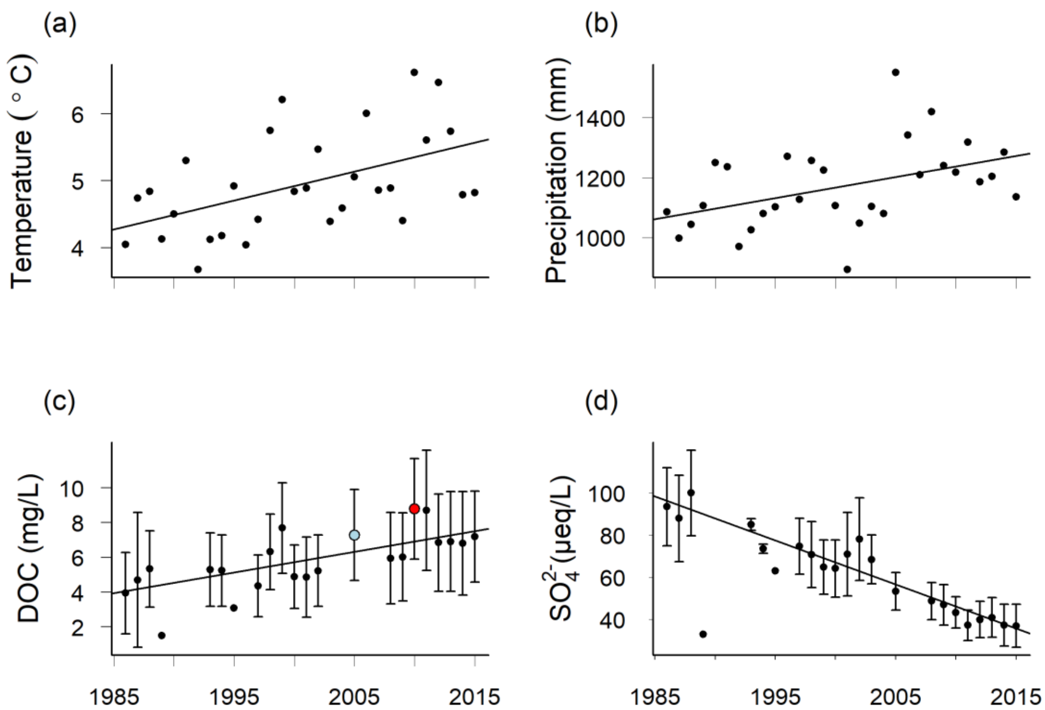

Figure 1.3. Trends for climate and water chemistry variables. a) Annual mean temperature in ˚C for the high elevation lake region in Maine from 1986-2015. Linear regression line shows significant trend (p = 0.004). b) Annual precipitation in mm per year in the high elevation lake region in Maine from 1986-2015. Linear regression line shows significant trend (p = 0.013). c) Mean dissolved organic carbon (DOC) concentration for all lakes from 1986-2015. The blue circle represents the wettest year, and the red circle represents the warmest year. (p = 0.0001). d) Mean sulfate concentrations for all lakes from 1986-2015. Sulfate was log transformed for analysis, but the untransformed concentrations are presented in this figure for ease of visual interpretation. Linear regression line shows significant trend (p < 0.0001). Error bars represent ± 1 standard deviation.

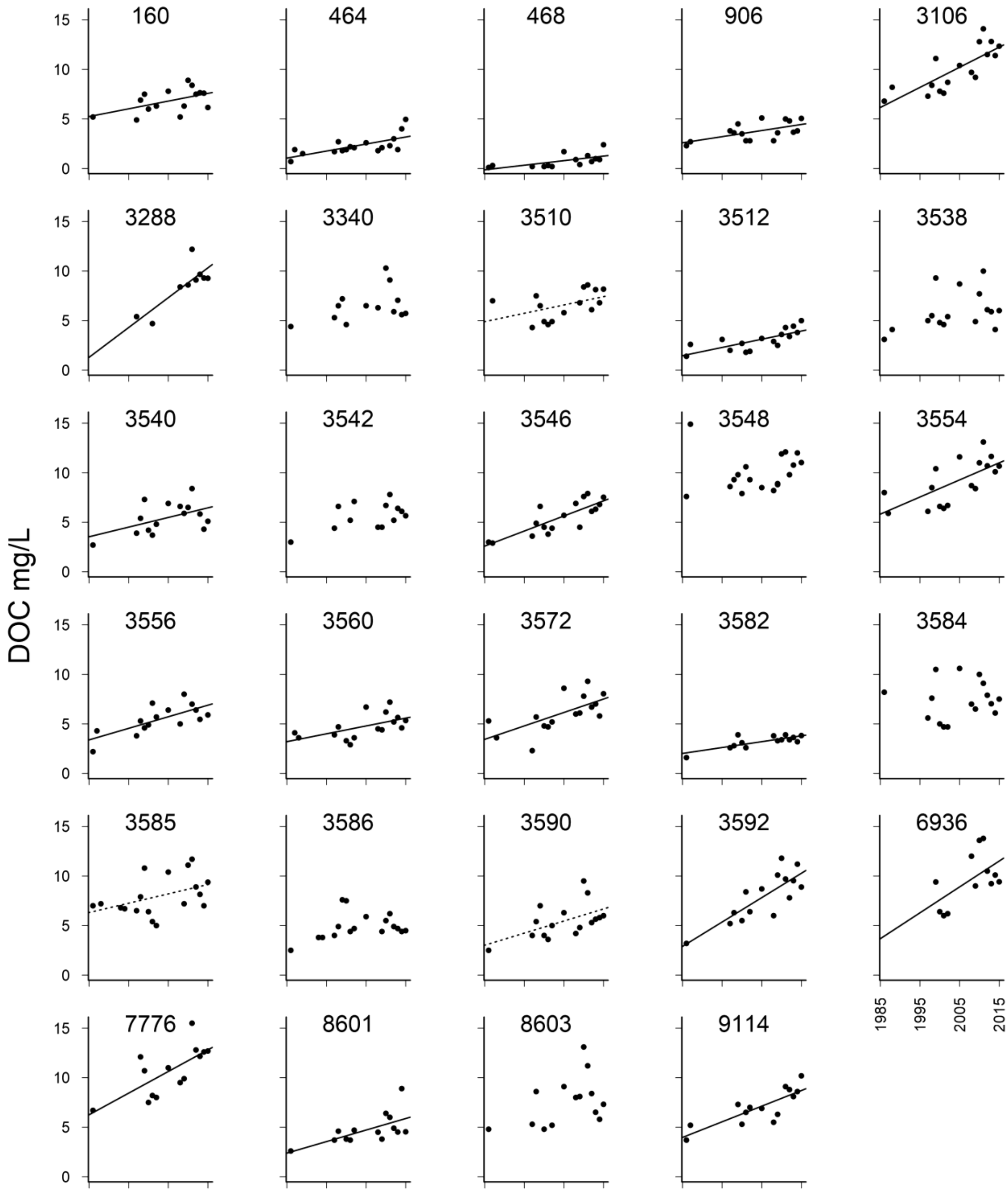
DOC mg/L
160
464
468
906
3106
3288
3340
3510
3512
3538
3540
3542
3546
3548
3554
3556
3560
3572
3582
3584
3585
3586
3590
3592
6936
7776
8601
8603
9114
0
5
10
15
1985
1995
2005
2015

Figure 1.4. Continued. Dissolved organic carbon (DOC) concentrations from 1986 to 2015 for the 29 high elevation lakes used in this study. Each subplot is identified using a four digit MIDAS number, a unique identification number assigned to all ponds and lakes in Maine. Axis labels are on the left and bottom plots. Solid linear regression lines are shown for significant trends ($p < 0.05$), and dotted linear regression lines are shown for trends that are significant at ($p < 0.1$).

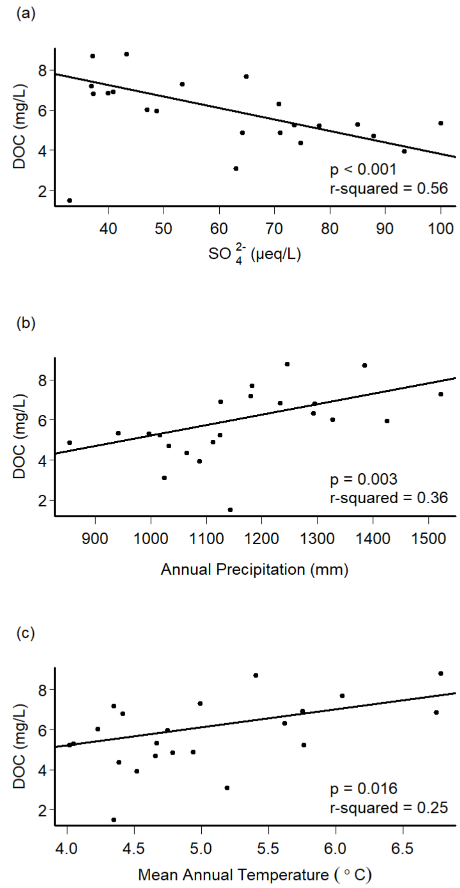

Figure 1.5. Linear regression analyses between DOC and SO42-, annual precipitation, and mean annual temperature in the high elevation lake region in Maine from 1986 – 2015. a) DOC regressed with SO_4^{2-} showing a significant negative trend. SO_4^{2-} was log transformed for analysis, but the untransformed data are plotted. b) DOC regressed with annual precipitation in mm in the 12 months prior to sampling shows a significant, positive trend. c) DOC regressed with annual mean temperature in ˚C in the 12 months prior to sampling shows a significant, positive trend.

DOC, mean annual air temperature, and total annual precipitation all increased linearly during the project period, and SO_4^{2-} concentrations decreased incrementally over time. Although it is difficult to disentangle the effects of recovery from acidification (indicated by declining SO_4^{2-}) and climate change on DOC (Figure 1.3.), we used linear regression to individually evaluate the relationship of each of these potential drivers with DOC. DOC was positively correlated with annual precipitation ($p = 0.003$, $r^2 = 0.36$) and mean annual temperature ($p = 0.016$, $r^2 = 0.25$) and negatively correlated with SO_4^{2-} concentrations ($p < 0.001$, $r^2 = 0.56$) (Figure 1.5.). Linear regression revealed inverse, significant relationships between net changes in DOC and net changes in SO_4^{2-} concentrations in the HELM and RLTM lakes ($p = 0.009$, $r^2 = 0.24$ and $p = 0.0004$, $r^2 = 0.62$ respectively) (Figure 1.6.).

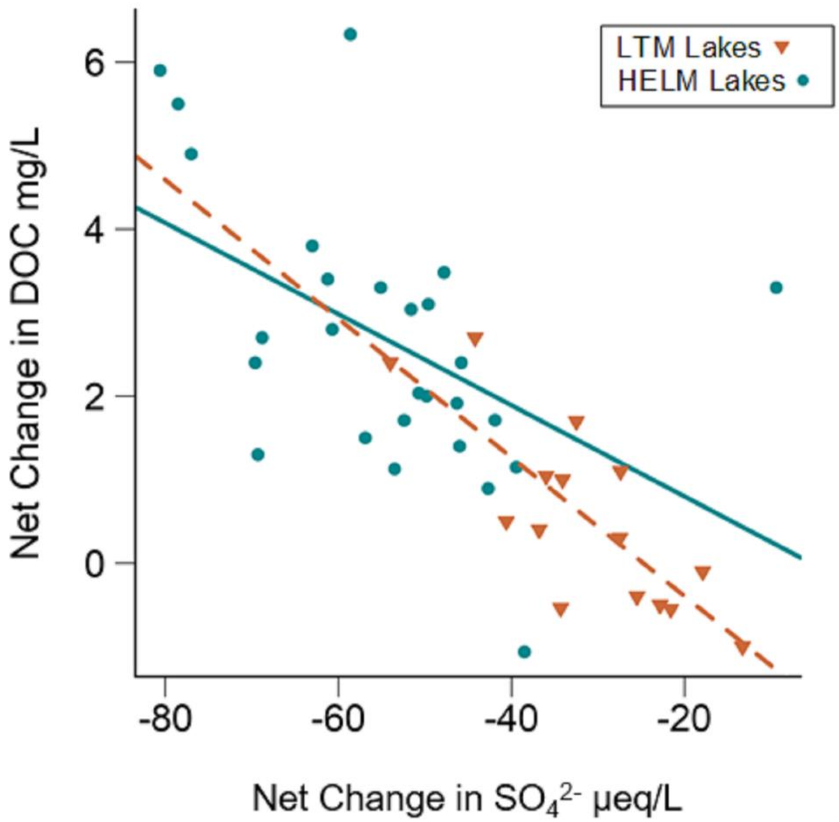

Figure 1.6. The net change in SO42- regressed with the net change in DOC for each lake. Net change was calculated by subtracting the median chemical concentration during the three most recent years of sampling from the median SO_4^{2-} concentration during the first three years of sampling. High Elevation Lake Monitoring (HELM) lakes are represented using green circles. Linear regression for significant HELM lake trend is shown with a green, solid line. Lower elevation, Regional Long-Term Monitoring (RLTM) lakes are orange, inverted triangles. Linear regression for significant RLTM lake trend is shown with an orange, dashed line.

Using both HELM and RLTM lakes in an analysis of net changes in DOC and SO_4^{2-} allowed a direct comparison of biogeochemical trends in high elevation and lower elevation lakes. Changes in RLTM lake water chemistry ranged from -1.0–2.7 mg/L for DOC and from -54.0-13.3 μeq/L for SO_4^{2-}. Mean DOC net change for all RLTM lakes was 0.5 mg/L, and mean net change in SO_4^{2-} was -31.2 μeq/L. With a range of net change in DOC from -1.1-6.3 mg/L and mean net change of 2.8 mg/L, changes in DOC were greater in HELM lakes than in RLTM lakes. DOC increased in 10 of 15 RLTM lakes compared to 27 of the 28 HELM lakes. It is worth noting that although Round Pond (MIDAS number 3584) had a -1.1 mg/L net change in DOC, the overall trend line for this lake is positive (Figure 1.4). In HELM lakes, the range of net change range, 80.6 to -9.4 μeq/L, and mean change, -54.4 μeq/L, of SO_4^{2-} are greater than those for RLTM lakes.

During 1997, the HELM lakes in this study were sampled in both October and November, which provided insight into the monthly variation and changing DOC concentrations following a large rain event. The total rainfall delivered to Maine's high elevation lake region in October 1997 was only 34% of mean October rainfall since 1895. Mean DOC concentrations of all lakes in October 1997 was 4.4 mg/L. With 116 mm of rain, November was the wettest month of the year, and mean November DOC concentrations across all lakes rose to 7.7 mg/L, a 3.3 mg/L increase in mean DOC concentrations in a single month.

There was a weak, negative relationship between annual mean temperature and DOC CV (p = 0.1, r^2 = 0.25) (Figure 1.7.). Linear regression with mean monthly temperature revealed that mean September temperature was the strongest predictor of DOC CV (p= 0.005 and r^2 = 0.40). The regression for July resulted in a weak relationship (p= 0.1 and r^2 = 0.16), and no other months had a significant relationship with DOC CV. Except for April and October, mean temperature of all months had inverse, but not significant, relationships with DOC CV. Linear regression of DOC CV with mean March-September temperature (p = 0.07 and r^2 = 0.28) and with May-September temperature (p = 0.02 and r^2 = 0.19) both

demonstrated an inverse and significant, or nearly significant, relationship. Results from temperature and time regressions are summarized Appendix Table 3. DOC CV was also regressed with annual and monthly precipitation values, but no regression results were significant.

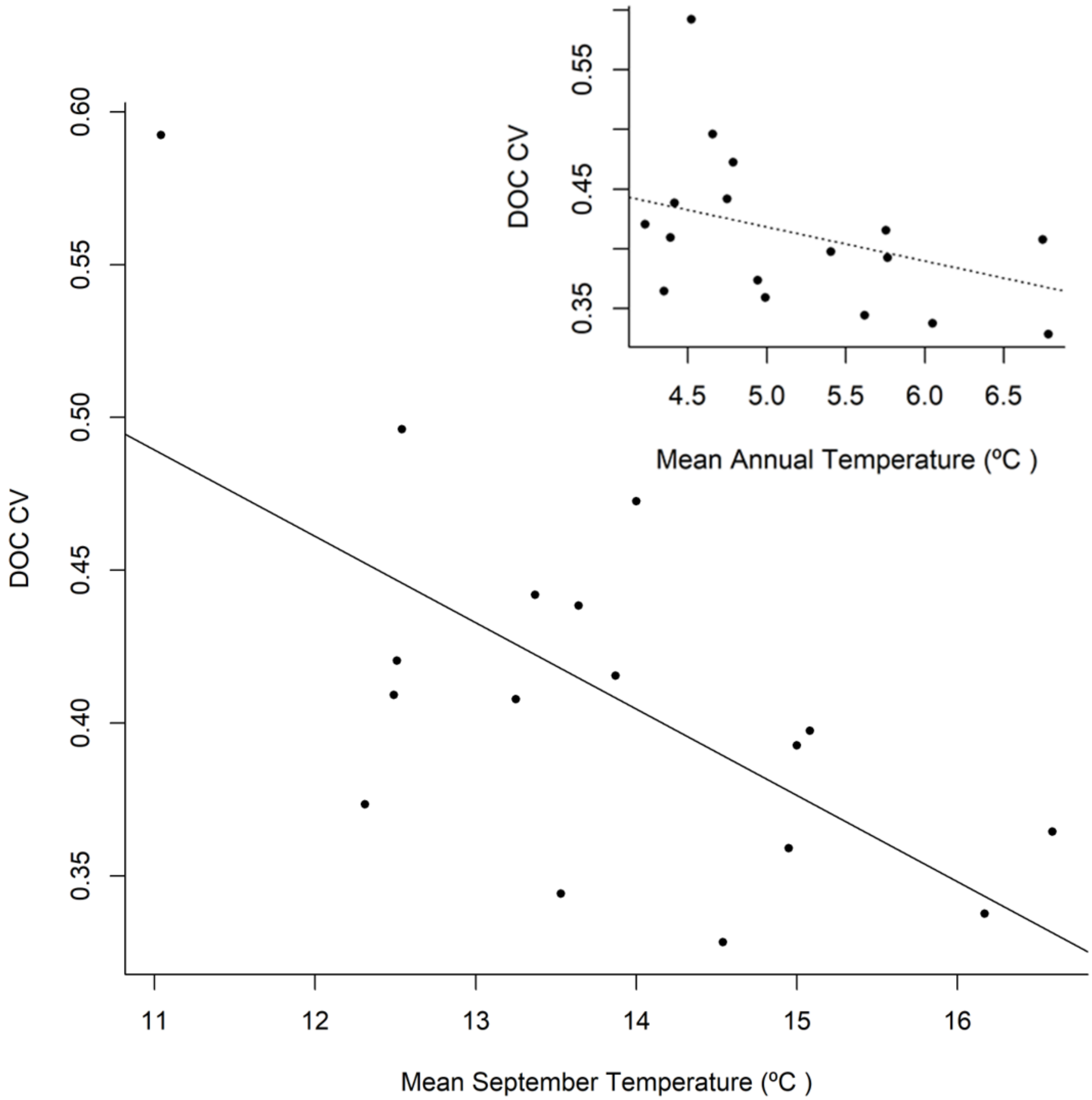

Figure 1.7. Coefficient of variation (CV) of the DOC concentrations in the 29 lakes in a given year as a function of mean September temperature for each year in ˚C. Linear regression shows a significant trend. The smaller inset shows the coefficient of variation of the DOC concentrations in the 29 lakes in a given year as a function of mean annual temperature in ˚C calculated for the 12 months prior to November of the sample year. The dotted line represents the linear regression line.

The LMER model quantified the strength of SO_4^{2-} and climate effects on DOC concentrations while controlling for the variability among individual HELM lakes (Table 1.1.). This model accounted for 78% of the variability in DOC ($r^2 = 0.78$). The strongest predictor of DOC concentration was an inverse relationship with SO_4^{2-} concentrations, followed by fall precipitation, then air temperature. Summer precipitation and spring air temperature were also significant, but their estimates show less predictive power than SO_4^{2-} and fall climate variables.

	Scaled Estimates	*p* - value	r^2
log SO_4^{2-}	**-0.361**	**0.000**	
Fall Precipitation	**0.135**	**0.000**	
Fall Temperature	**0.112**	**0.002**	
Summer Precipitation	**-0.065**	**0.012**	
Summer Temperature	-0.009	0.841	
Winter Precipitation	0.048	0.073	
Winter Temperature	0.032	0.293	
Spring Precipitation	-0.004	0.866	
Spring Temperature	**0.074**	**0.003**	
			0.78

Table 1.1. Estimates and significance of SO42- and climate variables on DOC, evaluated by a linear mixed effects model. The scaled estimates represent the number of deviations change in DOC per unit change of the respective variable. The Wald Test was used to determine significance of fixed effects variables. Significant variables are highlighted in bold.

Discussion

Compared to other studies in the northeastern US, the HELM lakes show the strongest, most consistent increases in DOC (Figure 1.4.), suggesting a greater and more regionally uniform increase in DOC than in lower elevation lakes in the northeastern US, where long-term trends in DOC were variable (Brown et al., 2017; Driscoll et al., 2016; SanClements et al., 2012; Strock et al., 2016). As of 2012 reporting, five of nine Maine RLTM lakes (56%) had significant increasing trends in DOC (Brown et al., 2017; SanClements et al., 2012). *Strock et al.,* [2014] summarized DOC trends in 74 US EPA LTM network lakes across Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, and southern New York, ranging in elevation (sea level – 750 m asl), lake area (2 – 600 ha), and landscape setting, and found that only 9% of the lakes had significant long-term increases in DOC (7 of 74 lakes). In a set of lakes in New York's Adirondack Mountains (lake area ranged from 1.2-187 ha; elevation ranged from 381-873 m), *Driscoll et al.,* [2016] found that DOC increased in 29 of 48 lakes (60%) and significantly decreased in two of the lakes (Baldigo, Roy, & Driscoll, 2016).

Due to climatic factors at high elevations, bedrock geology with little ANC, frequent immersion in acidic cloud, and dominant softwood forest cover, high elevation lakes were more vulnerable to acidification and experienced higher levels of acidity than other New England lakes (Aleksic et al., 2009; Baumann, 2011; Gerson, Driscoll, & Roy, 2016; Greaver et al., 2012; Weathers, Lovett, Likens, & Lanthrop, 2000). Coupled with higher amounts of precipitation, HELM lakes were more influenced by acidic deposition than other lake subsets in Maine (Kahl, 1998). A study in the Catskill Mountains of New York State showed that lakes above 1000 m had 13-40% higher rates of S deposition than nearby low-elevation sites during the height of acidification (Weathers et al., 2000).

Dramatic changes in atmospheric chemistry occurred in response to a congressionally mandated decrease in SO_2 emissions from power-generation sources, and these changes are strongly

associated with increased DOC concentrations in high-elevation lakes. SO_4^{2-} concentrations in precipitation have been reduced in northeastern US by 70% between 1980-2010 and the subsequent reduction of SO_4^{2-} represents a return to nearly pre-industrial (~ 30 μeq/L) concentrations ca. 100 years ago (Davis, Norton, Hess, & Brakke, 1983; Kahl, 1998; Strock, Nelson, Kahl, Saros, & McDowell, 2014; Wright, 1988). SO_4^{2-} deposition increases ionic strength of soil solutions, which slows the DOC flux from terrestrial ecosystems (Monteith et al., 2007). The counter mechanism results in an increased rate of terrestrial DOC flux under less acidic conditions (de Wit et al., 2016; Ekström et al., 2011; Evans et al., 2006; Hruška et al., 2009; Lawrence, Simonin, Baldigo, Roy, & Capone, 2011; Monteith et al., 2007; SanClements et al., 2012; Sawicka et al., 2017). This study demonstrates a strong inverse relationship between net changes in SO_4^{2-} and DOC, which supports the argument that recovery from acidification is an important driver of long-term increasing DOC trends in this region. These results are supported by a 15-year study in Scandinavia that found the strongest trends for increasing DOC occurred in regions that experienced robust reduction in SO_4^{2-} (de Wit et al., 2016) This study also provides evidence for the likely complexity of underlying mechanisms driving the DOC trends, since climate variables were also strongly correlated with DOC, although less so than SO_4^{2} (Figure 1.5. and Figure 1.6.).

These physical and chemical properties of acid-sensitive HELM lakes explain the greater amounts of initial SO_4^{2-} deposition, which allowed for a greater net change in SO_4^{2-} concentrations than of lower elevation lakes. To put the biogeochemical trends observed in high elevation lakes into spatial perspective and strengthen the comparison of high elevation lakes with lower elevation lakes, we directly compared DOC and SO_4^{2-} trends in HELM and RLTM lakes, both sampled by the same research team. Lower elevation lakes had lower peak SO_4^{2-} concentrations and more variable DOC trends than high elevation lakes. Only 66% of the lower elevation lakes revealed net increases in DOC, compared to 96% of HELM lakes. These trends demonstrate that the extent of acidification in both high and low elevation lakes is correlated with increasing DOC trends and greater decreases in SO_4^{2-} are correlated

with greater increases in DOC. Therefore, population wide increasing DOC concentrations in HELM lakes shows a relatively stronger sentinel response to acidification in high elevation lakes than lower elevation lakes. A meta-analysis of high elevation lakes in the northeastern US could help determine if high elevation lakes in general experience stronger trends for increases in DOC than lower elevation lakes.

Anomalies in the SO_4^{2-} concentrations of one of the HELM lakes exemplify a deviation from the linear relationship between the change in SO_4^{2-} and change in DOC (Figure 1.6.). Peak SO_4^{2-} concentrations of Greenwood Pond never surpassed 35 µeq/L, a concentration that is lower than the 2013-2015 median concentrations of 17 of 29 HELM lakes and comparable to pre-industrial SO_4^{2-} concentrations (Wright, 1988). Increasing DOC trends in Greenwood Pond, despite a lack of acidification and subsequent recovery, provide additional evidence that acidification is not the only driver of increased DOC in these lakes.

In a study of predominantly lower elevation lakes in northeastern US, *Strock et al.,* [2016] observed positive DOC deviations during an extreme wet year. *Strock et al.,* [2016] reported regional DOC increases between 0.5 and 1.0 mg/L in 2005, the wettest year of the 1990-2010 study period, compared to the study period average. Mean DOC concentration of all HELM lakes in 2005 was 1.0 mg/L greater than mean DOC concentrations for the entire HELM study period (Figure 1.3.c), which is consistent with the findings of *Strock et al.,* [2016]. In the Adirondack Mountains in New York, the amount of DOC transported from the watershed to receiving lakes was positively correlated with total annual rainfall, and the wettest year of the study exported the most DOC (Canham et al., 2004). Conditions characterized by large amounts of rainfall and subsequent soil saturation cause the dominant runoff flow path to rise from lower mineral soil horizons that absorb DOC to surface, organic carbon-rich soils and flushing of DOC to nearby water sources (Boyer et al., 1996; Clark et al., 2005; Couture et al.,

2012; de Wit et al., 2016; Evans et al., 2006; Jennings et al., 2012; McDowell & Likens, 1988; Neff & Asner, 2001; Reche & Pace, 2002; Strock et al., 2016).

Although there is support for an increase in DOC concentrations during wet years in HELM lakes, DOC response to the wettest year of the study period (2005) was not extraordinary. The mean DOC concentration for the wettest year of the study period was 7.3 mg/L, which represents only the fourth highest mean DOC concentration in the study period (Figure 1.3.c). The highest mean DOC concentration for the entire study period occurred during the warmest year, 2010 (Figure 1.3.a); however, mean DOC concentrations in 2011 were almost identical to 2010. The variability among years with high DOC concentrations suggest that more parameters, like long-term climate change and acidification, in conjunction with weather events are driving trends in DOC.

The 1997 precipitation case study demonstrated a large increase in DOC (from 4.4 mg/L to 7.7 mg/L) after one heavy precipitation month that had relatively dry antecedent conditions. Although this dataset lacks higher frequency sampling to fully understand this event and others like it, it demonstrates that precipitation and drying-wetting cycles affect DOC patterns in HELM lakes. Similar events have been researched in a high elevation lake in California's Sierra Nevada mountains, where DOC concentrations nearly doubled and an entire season of terrestrial DOC was flushed from the lake catchment in response to an autumn rain event (Sadro & Melack, 2012). The drastic change from net autotrophic to net heterotrophic conditions could induce hypoxic or anoxic conditions under ice (Sadro & Melack, 2012). *Sadro and Melack* [2012] also hypothesized that if a storm of similar magnitude had occurred earlier in the ice-free season or soon after spring mixing, the consequences could have longer-term effects on metabolic lake balance. A dramatic spike in DOC concentrations was also observed in Canadian boreal lakes after 90% of mean summer precipitation fell in a four day rain event (Couture et al., 2012). Similar studies in larger, deeper, low elevation lakes in Pennsylvania demonstrate a significant DOC

concentration response to precipitation after 60 days in an intermediate DOC lake and no significant response in a clear, low-DOC lake (Williamson et al., 2014). Our case study suggests that interannual variability of DOC in HELM lakes can be attributed to patterns in weather events, antecedent conditions, and drying-wetting cycles (Christ & David, 1996; Couture et al., 2012; Dawson et al., 2008; M Gödde et al., 1996; Raymond & Saiers, 2010; Zhang et al., 2010). Depending on the timing, frequency, and magnitude of events, changing patterns in weather could contribute to long-term increases in DOC concentrations (Boyer, Hornberger, Bencala, & Mcknight, 1997; Raymond & Saiers, 2010; Strock et al., 2016; Williamson et al., 2014). Higher frequency sampling could put this finding into context and help decipher patterns in antecedent conditions, individual weather events, and the duration of episodic DOC increases.

Results from the linear mixed effects model allowed us to explore the effects of seasonal weather on DOC concentrations (Table 1.1.) and showed that autumn precipitation and air temperature were the strongest climate predictors for DOC concentrations. Because samples for this study were always collected in October and November, it is not surprising that autumn climate was the most effective in driving DOC concentrations, in accord with previous work by *Williamson et al.*, [2014], who showed that lake DOC concentration responded to changes in precipitation and temperature at time scales of 30-75 days.

Our data suggest that the warmer and drier drought years could influence the DOC-SO_4^{2-} relationship by promoting the oxidation of S to SO_4^{2-} and increasing export of SO_4^{2-} from soils to lakes. The suppression of DOC concentrations that characterizes drought conditions has been attributed to increases in terrestrially derived SO_4^{2-} (Clark et al., 2005; Kerr et al., 2012; Strock et al., 2016). Despite an overall positive correlation between mean annual temperature and DOC (Figure 1.5.), warm summer temperatures during 2001-2004 drought years reversed the correlation between DOC and temperature. Only one other drought during the last century, spanning 1965 and 1966, had comparable severity to

the drought of the early 2000s (Strock et al., 2016). Furthermore, the pulses of surface water SO_4^{2-} that occur during droughts contribute to episodic acidification, which could hinder lake recovery from acidic deposition (Kahl et al., 1992; Kerr et al., 2012; Stoddard et al., 1999; Strock et al., 2016; Watmough, Eimers, & Baker, 2016). Defining the underlying mechanisms driving the linkage between weather variables and lake chemistry provides insight for understanding the intra- and inter- annual variability in DOC concentrations and how different lake processes respond to both weather and long-term climate trends (Raymond & Saiers, 2010; Strock et al., 2015).

Inverse relationships between the CV of DOC concentrations and air temperatures across a variety of temporal scales suggests that higher air temperatures result in decreased variability in DOC concentrations across HELM lakes (Figure 1.7.). Mean September temperatures were most strongly correlated with DOC CV, suggesting that these higher temperatures resulted in more homogeneity in the processes that control DOC concentrations. Mean temperature for October was not significantly correlated with DOC CV, so it is unlikely that these results are only driven by September's proximity to sample dates.

Lower variability in DOC concentrations during warmer years could indicate a temperature-based mechanism across the entire system or reflect fewer or less complex DOC sources from the watershed. Studies across North America have demonstrated that terrestrially derived DOC overwhelmingly contributes to the DOC pool in small, temperate lakes [Reche and Pace, 2002; Raymond and Saiers, 2010; SanClements et al., 2012; Read and Rose, 2013; Williamson et al., 2014]. Under certain soil moisture conditions, higher air and soil temperatures increase biological activity in terrestrial zones, which results in more decomposition and availability of organic matter and DOC solubility [Christ and David, 1996; Gödde et al., 1996; Dawson et al., 2008; Raymond and Saiers, 2010]. In the forested Bear Brook Watershed in Maine, air and soil temperatures were similar, particularly during late summer and

early autumn, so we infer that patterns in air temperatures during September are a reasonable proxy for soil temperatures (Fernandez, Karem, Norton, & Rustad, 2007). Warmer temperatures, in conjunction with decreasing atmospheric SO_4^{2-} deposition, could be driving increased terrestrial DOC input to lakes via more production and enhanced solubility. Results from peat soil studies in the UK indicated that temperature, along with declining SO_4^{2-} deposition, exerted significant effects on long-term increases in DOC (Evans et al., 2006).

The relationship of September temperature and DOC variability could also relate to the strength of a particular year's wetting and drying cycle (Christ & David, 1996; Dawson et al., 2008; Naden et al., 2010). Increasing microbial activity in warmer Septembers could contribute to a larger source of organic carbon available for transport (Dawson et al., 2008). Soil chemistry models demonstrate that observed global DOC increases are unlikely to have occurred under a warming-only scenario and attribute increasing DOC trends to the synergy of changing atmospheric deposition and increasing temperatures (Sawicka et al., 2017). Other studies predict that the influence of temperature on DOC concentrations will become more significant, and DOC concentrations could increase 20-89% under different warming scenarios (Futter et al., 2011; Naden et al., 2010). It is expected that temperature in the northeastern US will continue to increase. Heat waves are predicted to occur more frequently, with greater intensity, and for a longer duration, so these results are particularly relevant to the effects of climate change on biogeochemical processes in this region (Horton et al., 2014).

Decreasing DOC variability suggests that temperature-induced DOC fluxes are occurring across Maine's HELM region and the lower variability of DOC in warmer years is an indicator that, regionally, these HELM systems are affected by rising temperatures. The collinearity of increasing DOC and increasing temperature and the strength of the SO_4^{2-} signal in HELM lakes complicates understanding the roles of individual drivers on DOC (Figure 1.5.). Strong relationships between the variability of DOC

and temperature indicate that the variability of a chemical could be a useful tool for detaching confounding parameters. We are unaware of another study that has considered biogeochemical variability as a proxy for the presence of a mechanism, so future exploration of temperature and DOC variability in similar systems is promising. The homogenization of variability in DOC concentration in response to warmer temperatures could have implications for prediction and modeling of future DOC responses and trends.

Results from the linear mixed effects model show that together, climate and lake SO_4^{2-} concentrations explain over 75% of the variability in DOC concentrations (Table 1.1.), with lake SO_4^{2-} as the single most important variable. The scaled estimates from the linear mixed effects model suggest that, although seasonal precipitation and temperature alone may not explain a large portion of DOC concentrations, when considered together, these results strongly suggest that climate is contributing to increasing DOC trends (Table 1.1.).

Regardless of the mechanism for DOC increases, a population-wide transition from historically low-DOC lakes to intermediate-DOC lakes has implications for the biological and physical properties of HELM lakes (Kahl, 1998). A study of arctic and boreal lakes demonstrated a nonlinear relationship between DOC concentrations and whole-lake primary production and identified 4.8 mg/L as an important biological threshold for relationships between DOC and primary production (Seekell et al., 2015). In systems where DOC was below the threshold, there was a positive relationship between DOC and primary production, while above the threshold the relationship was negative (Seekell et al., 2015). Similarity between landscape composition in Maine's HELM lakes and boreal lakes makes for reasonable extrapolation between systems; the observed population-wide shift of DOC in HELM lakes to above 5 mg/L could drastically reduce primary production in these lakes if further increases occur. In Maine RLTM lakes, changes in the diatom community composition are most pronounced in lakes with

increasing DOC (Brown et al., 2017). The implications for this could be far-reaching, as HELM lakes currently provide refugia for aquatic and macroinvertebrate communities that have declined in other places due to fish stocking, anthropogenic stressors, and climate change (Schilling, Loftin, Degoosh, Huryn, & Webster, 2008).

Due to increasing light attenuation, increases in DOC can reduce mixing depths and strengthen thermal stratification in small lakes (Brown et al., 2017; Effler, Schafran, & Driscoll, 1985; Fee, Hecky, Kasian, & Cruikshank, 1996). Multi-decadal DOC trends in Pennsylvania revealed more than a doubling of DOC concentrations in Lake Giles, and suggested that clear lakes are more sensitive to brownification than less transparent, higher DOC lakes (Williamson et al., 2015). In small lakes in Wisconsin and Michigan*, Read and Rose* [2013] found that lakes with lower DOC concentrations were more sensitive to temperature and suggested lakes with higher DOC concentrations were more buffered from increasing temperatures than clearer lakes. Results from our study highlight the importance of informed management decisions that will mitigate the vulnerability of Maine's high elevation lake region and other similar high elevation systems to anthropogenic stressors like climate change, air pollution, and land-use change.

High elevation mountain lakes have been described as regional and global sentinels that can act as early warning systems to environmental change (Battarbee, Catalan, Grytnes, & Birks, 2002; Strang & Aherne, 2015). Prior to industrially-induced atmospheric deposition and rapid climate change, freshwaters at high elevations were considered 'pristine' (Kahl, 1998). The HELM lakes provide a unique opportunity to serve as reference conditions for the northeastern US. Their wilderness setting provides a control for many local, in-watershed anthropogenic stressors. However, long-range atmospheric transport of contaminants and climate change are affecting these systems (Catalan & Donato Rondón, 2016). The HELM project provides 30 years of data supporting insight into this period of rapid change. Researchers can understand the implications of recovery from acidification by capturing the response of

SO_4^{2-} to the CAAA, but the implications of climate change on lake ecosystem stability have only recently been the subjects of intensive research.

The effects of climate change are expected to be amplified at high elevations, particularly at higher latitudes (Bradley, Keimig, & Diaz, 2004; Mast, Turk, Clow, & Campbell, 2011). Increased climate variability and precipitation are expected to increase faster in Maine's high elevation lake region than other biogeoclimatic zones (Fernandez et al., 2015). If atmospheric SO_4^{2-} deposition and its influence declines and climate increasingly controls surface water DOC concentrations, headwater systems that lack the heterogeneity of more complex and often larger landscape settings may be the 'canary in the coal mine' for understanding biogeochemical variability in a changing climate.

In this study, we found that most of the HELM lakes had significant increases in DOC concentration since the 1980s. Lake SO_4^{2-} concentrations, air temperature, and precipitation explained much of the variability of DOC concentrations. Mean SO_4^{2-} concentrations for HELM lakes were 38.5 μeq/L between 2013-2015 and are nearing pre-industrial concentrations. Thus, it is likely that SO_4^{2-} effects on DOC will weaken in the future, with an increasing role for climatic factors such as warming, drought, and the increasing frequency and intensity of extreme events. DOC concentrations in HELM lakes were positively correlated with mean annual air temperature and precipitation. We observed an inverse relationship between DOC variability among lakes and air temperature, suggesting increasing air temperatures could exert a regional effect on HELM DOC concentrations (Figure 1.7.). Our results also show a significant, positive relationship between precipitation and DOC concentrations, and results from measurements in October and November 1997 indicated that a single, large precipitation event can strongly influence DOC concentrations. These results highlight the importance of short and long-term precipitation patterns as a driver of lake DOC concentrations.

The Maine HELM lakes were originally chosen because they were acid-sensitive, sentinel sites. The lakes now serve as sentinels for climate change; as with other high elevation lake sites, they indicate sensitivity in DOC concentrations to changing precipitation patterns and warming temperatures. Long-term ecosystem monitoring will continue to be important in the future to build on the rich data set beyond recovery from acidification as we seek to understand the complexity of responses to multiple anthropogenic and natural drivers of change in these fragile, high elevation lake ecosystems.

CHAPTER 2

PHYSICAL AND CHEMICAL CONTROLS ON COLD-WATER REFUGIA IN SMALL NORTHERN TEMPERATE LAKES

Introduction

Multi-decadal trends of increasing dissolved organic carbon (DOC) in northern temperate lakes signal a period of change for aquatic ecosystems. Changes in DOC are twofold: not only are DOC concentrations increasing, the quality and source of the suite of molecules that comprise DOC are transitioning (Donahue, Schindler, Page, & Stainton, 1998; D.M. McKnight et al., 2001; Sanclements et al., 2018; SanClements et al., 2012). These trends are integrated signals of change from the surrounding air- and water-sheds and reflect the effects of large scale, multi-decadal changes in climate and atmospheric deposition (Adrian et al., 2009; Gavin et al., 2018; Williamson, Saros, Vincent, & Smol, 2009). In addition to representing a sentinel response to acidification and climate change, changes in DOC have important implications for biota and biogeochemical processes (de Wit et al., 2016; Evans et al., 2006; Monteith et al., 2007; SanClements et al., 2012; Williamson et al., 1999, 2009). Furthermore, understanding the changes in quality and quantity of DOC could be particularly relevant in smaller, oligotrophic, northern temperate lakes, where terrestrial DOC is the predominant driver of thermal structure. Changes in DOC quality and quantity may alter the availability of cold-water habitat in lakes and affect the resiliency of cold-water refugia to predicted increases in temperature and precipitation to the north temperate zones (Fernandez et al., 2015; IPCC, 2007; Janowiak et al., 2018; Salinger, 2005; USGCRP, 2017).

In the northern hemisphere, DOC is predominantly allochthonous, or derived from the terrestrial environment (Thurman, 1985; Winterdahl, Bishop, & Erlandsson, 2014). With the exceptions

of low-DOC or eutrophic lakes, autochthonous (microbial sourced) DOC is secondary (Morris et al., 1995; Winterdahl et al., 2014). Studies of DOC dynamics in north temperate lakes indicate that increasing DOC concentrations are concurrent with an increase in the relative input of terrestrial DOC (Donahue et al., 1998; D.M. McKnight et al., 2001; Sanclements et al., 2018; SanClements et al., 2012). This increasingly terrestrial signature of lake water DOC has been attributed to a decrease in soil acidity and the subsequent enhanced solubility and transport of dissolved soil organic matter to lake water, which signals recovery from anthropogenic acidification (Donahue et al., 1998; Monteith et al., 2007; Sanclements et al., 2018; SanClements et al., 2012). Increasing frequency and magnitude of rain events in North America are also linked to increasingly allochthonous DOC via flushing or saturation mechanisms (Dillon & Molot, 2005; Sanclements et al., 2018; Zwart, Sebestyen, Solomon, & Jones, 2016). Large rain events can increase the saturation of soils and raise the water table, promoting flow through organically rich soil shallow soils and flushing DOC into surface waters (Boyer et al., 1996; de Wit et al., 2016; Jennings et al., 2012; McDowell & Likens, 1988).

The yellow-brown color of humic and fulvic acids that compose allochthonous DOC imparts a stain in DOC-rich waters, a phenomenon referred to as “browning” (Wetzel, 1983; Williamson et al., 1999). In small, oligotrophic lakes that are wind protected, DOC-induced browning is the predominant driver of light penetration and thermal structure (Fee et al., 1996; Markfort et al., 2010; Pace & Cole, 2002; von Einem & Granéli, 2010; L. A. Winslow, Read, Hansen, & Hanson, 2014). A faster rate of light attenuation in darker lakes restricts heat accumulation to the epilimnion (Houser, 2006). Additionally, the shallower mixing depths and subsequent increased relative epilimnetic surface area to volume ratio of darker lakes instigate a negative feedback loop, where atmospheric exchange and diel air temperature cycles prevent heat from accumulating in the epilimnion and promote a cooler whole lake heat content (Bowling & Salonen, 1990; Houser, 2006). In contrast, solar radiation can penetrate deeper into the water column in clear lakes, so heat is more readily accumulated and stored in the hypolimnion

(Effler et al., 1985; Houser, 2006; Houser, Bade, Cole, & Pace, 2003). Along with changes in water clarity, a greater discrepancy between surface and deepwater temperatures, earlier onset of stratification, and reduction in mean annual wind speed have been associated with increases in stratification stability (Hadley et al., 2014; Houser, 2006; Richardson et al., 2017). In a study of 231 lakes across northeastern North America, lakes positioned at more northern latitudes showed the most rapid increases in the strength of thermal stratification between 1975 and 2012 (Richardson et al., 2017).

The quality of DOC could potentially have further implications for thermal stratification and temperature dynamics. Humic components of DOC that are derived from the terrestrial environment are highly colored, large molecules that can further impact light penetration and UV attenuation beyond bulk DOC concentrations (Donahue et al., 1998). The higher aromaticity of terrestrially-derived fulvic acids is correlated with darker colors, which absorb more visible and UV light than microbially-derived fulvic acids (Kothawala et al., 2014; McKnight et al.,1994). Multidecadal surface water trends and field experiments have shown greater magnitudes of change in water color than bulk DOC concentrations over time and have attributed this to a change in the quality of DOC (Ekström et al., 2011; Erlandsson et al., 2008; McKnight et al., 2001).

Although studies show that deepwater temperatures are not changing in small, north temperate lakes, the size and persistence of the hypolimnion and subsequent availability of cold-water refugia could be affected by brownification (Richardson et al., 2017; L. A. Winslow et al., 2014). Warren at al. (2016) hypothesized that recovery from acidification in small, temperate lakes will give rise to larger, cooler hypolimnia. When considering the effect of changing DOC regimes and rising temperatures on small lakes in Wisconsin and Michigan, Read and Rose (2011) used temperature stratification data from eight lakes to build a water temperature model. They predicted that lakes with a 50% increase in DOC from baseline concentrations would be > 2˚C colder than lakes with a 50% reduction in baseline DOC

(Read & Rose, 2013). Richardson et al. (2017) noted the implications for changing hypolimnia volumes on fisheries, for the heat that accumulates in compressed and disappearing hypolimnia pose a threat to cold-water fish species.

We are unaware of any research that explores the changes in hypolimnion size and temperature in the context of changing DOC concentrations. In this study, our goal is to determine how DOC controls the size and persistence of the hypolimnion throughout the course of summer stratification. We hypothesized that lakes with higher DOC concentrations will exhibit a higher ratio of hypolimnion volume: total lake volume, and therefore have a larger volume of cold-water refugium that is less likely to warm or disappear over the course of a summer stratification period. Instead of differentiating between clear and dark lakes, we use quantifiable DOC concentrations and DOC quality metrics as proxies for light attenuation.

This research puts physical lake research into the context of biogeochemical trends and considers how alterations to DOC quality and quantity, sentinel responses to anthropogenic acidification and climate change, could affect the availability of cold-water habitat. By understanding the controls on DOC quality and quantity and its interactions with watershed and characteristics on the relative size and persistence of hypolimnia in small, north temperate lakes, we can begin to consider which chemical and physical parameters may define resiliency.

Materials and Methods

The lakes in this study are a subset of the RLTM (regionalized long-term monitoring) project in Maine. The total RLTM project consists of 16 acid sensitive lakes that have experienced little anthropogenic disturbance beyond atmospheric deposition (Kahl, Stoddard, Deviney, Webb, & Murdoch, 2004; Stoddard et al., 1999). We have selected eight of the 16 original lakes that represent a

range of DOC concentrations, multi-decadal trends, and landscape heterogeneity. The eight instrumented lakes will be referred to as RLTM -Temperature (RLTM-Temp) lakes for the rest of this paper. Of the eight RLTM-Temp lakes, seven lay within a 112-km radius of each other in eastern Maine (Figure 2.1.). The outlier is Bean, which lies in the western mountains of Maine. RLTM-Temp lake elevations range from 95 to 405 m, with a median elevation of 139 m. Median lake surface area is 125000 m^2 and ranges from 40,000 to 240,000 m^2. Watershed ratio, the ratio of lake area to total watershed area, ranges from 3.2 to 36.7, with a median of 11. RLTM-Temp lakes are predominantly drainage lakes but include two seepage lakes (Bracey and Crystal), here defined as lakes with no inlets (Kahl, 1998). Mixed deciduous-coniferous stands dominate the forests.

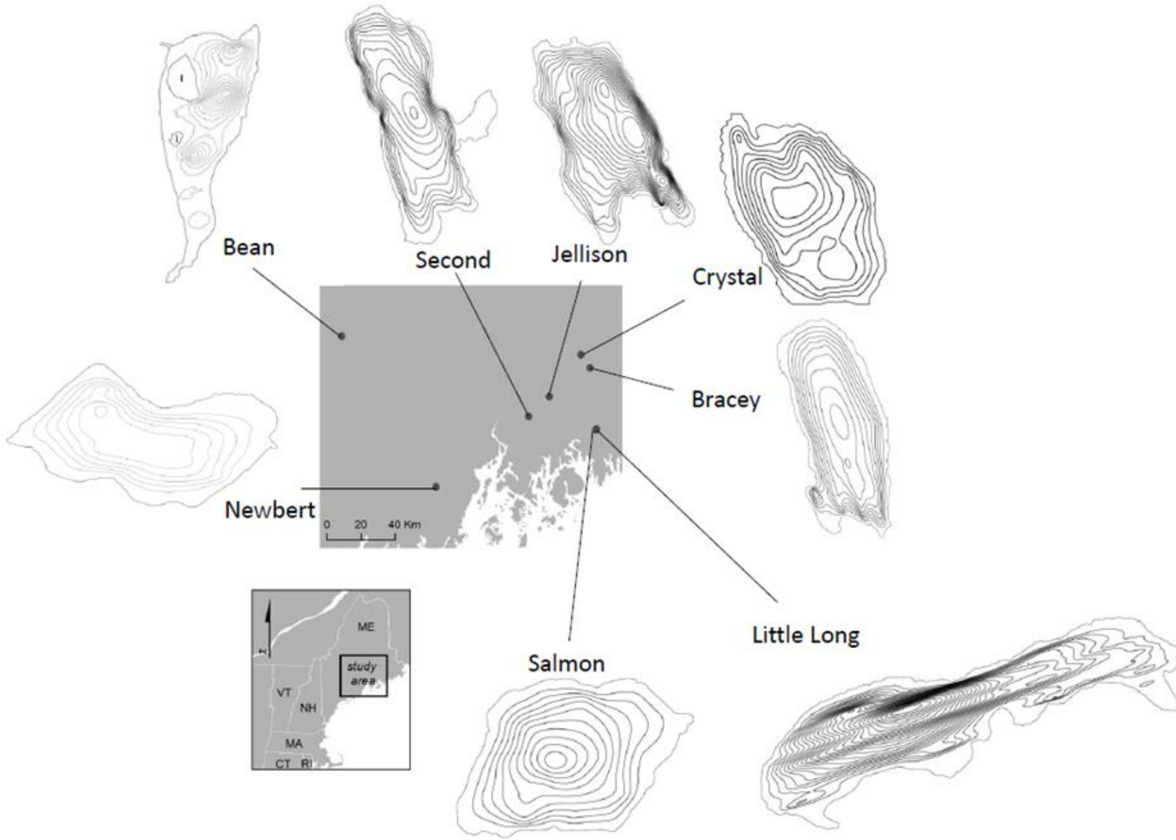

Figure 2.1. Location and bathymetry of eight lakes in this study, a subset of Regional Long-Term Monitoring lakes in Maine. Bathymetry lines are at 1-meter intervals for all lakes. The letter “I” indicates island location. Lake surface area is not to scale and documented in Table 2.1.

Lake Name	Lake Area	Avg. Elevation	Max. Depth	Lake Volume	Surface Depth Ratio	Avg. Slope	Wetland	Watershed	Watershed Ratio
	m^2	m	m	m^3		%	m^2	m^2	
Crystal Pond	100000	121	9	89401	11111	6.4	0	316800	3.2
Bracey Pond	80000	129	9	81107	8889	4.6	110000	912600	11.4
Little Long Pond	240000	148	25	259098	9600	24.2	50000	2167200	9.0
Salmon Pond	40000	105	10	25699	4000	13.8	0	148500	3.7
Jellison Hill Pond	180000	172	17	131285	10588	15.3	30000	2230200	12.4
Second Pond	270000	163	13	217353	20769	15.8	210000	2940300	10.9
Newbert Pond	130000	95	4	120916	32500	--	1570000	4766570	36.7
Bean Pond	120000	405	9	121142	13333	10.3	40000	1404900	11.7

Table 2.1. Watershed characteristics for eight Regional Long-Term Monitoring-Temperature lakes in Maine that were used in this study.

Lake geochemistry samples were collected from the epilimnion in pre-cleaned HDPE bottles and syringes (for closed-system pH), at ~0.5 m depth. Hypolimnion samples were collected early in the study period and again during the summer 2017 at ~0.5 m up from the bottom of the lake, using a Kemmerer sampling device and decanted into the same types of sampling containers as for epilimnion samples. All samples were collected from nonmotorized boats. Samples were placed on ice and returned to the University of Maine or University of New Hampshire analytical laboratories at the end of each sampling day. Sampling methodology was consistent with that described in *Strock et al.,* [2014] and *Kahl et al.,* [2004]. In 2017, fluorescence samples were collected separately in ashed amber class bottles, placed in dark coolers on ice for transport, refrigerated, and filtered. DOC quality analysis consisted of Fluorescence Index (FI), Specific ultraviolet absorbance ($SUVA_{254}$), Humification Index (HIX), and freshness (Weishaar et al., 2003). Fluorescence samples were sent to the University of Colorado Institute of Arctic and Alpine Research (INSTAAR) and methodology was consistent with that described in SanClements et al., 2012.

In May 2017, eight lakes were instrumented with a chain of thermistors (Onset HOBO Pendant). With the exception of Bean, instrumented lakes were within the same climate division, Southern

Interior, which minimizes the effect of varying weather on water temperature (Fernandez et al., 2015). Thermistors were placed at 1 m intervals throughout the water column at the deepest part of the lake and collected hourly temperature recordings. The deepest lakes (Little Long, Jellison, and Second) were not instrumented at every 1m. Instead, we used prior peak summer stratification data to predict epilimnion, metalimnion, and hypolimnion depths and instrumented at 1m intervals throughout the epilimnion, metalimnion, and placed probes at the top and bottom of the hypolimnion. Additionally, two probes were damaged in the field, so Newbert is missing the 3 m depth and Crystal is missing the 2 m depth.

All manipulations of thermal stratification data were done using the package "rLakeAnalyzer" (L. Winslow, Read, Woolway, Brentrup, & Zwart, 2017). The hypolimnion is defined as the first depth below the metalimnion (temperature change ≥ 1˚ C per meter) where temperature change is ≤ 1˚ C to the bottom of the lake. Using lake bathymetry maps, we were able to estimate the volume at each depth and subsequently the total volume of the hypolimnia. We calculated the hypolimnion volume ratio (HVR) as the ratio of the hypolimnion volume to the total lake volume for each lake. We calculated this for each day during the summer stratification period, defined here as June 1 to September 1. Volume-weighted hypolimnion temperature (VWHT) was calculated using rLakeAnalyzer and the daily HVR value. In some lakes, the hypolimnion disappeared (Crystal, Salmon, and Newbert), so the bottom temperature replaced the VWHT. We calculated the percent change of HVR of the hypolimnia over the course of summer stratification as the initial HVR minus the final HVR, divided by the initial HVR. Schmidt stability, a metric to describe the resistance to mechanical mixing, was used to quantify the strength of stratification throughout the water column and was calculated using "rLakeAnalyzer" (L. Winslow et al., 2017).

All statistical analyses were conducting in R software 2.12.1 (R Development Core Team, 2011). To assess temporal change in multi-decadal DOC trends, Mann-Kendall nonparametric tests were used, and trends were considered significant if $p \leq 0.05$. With the exception of Little Long, all lakes were sampled for chemical analyses three times per year in the spring, summer, and fall. Little Long was sampled seasonally until the late 1980s and continued as fall only sampling thereafter. Little Long was sampled seasonally again in 2017 for this study. To check for consistency when comparing lakes with seasonal samples and lakes with fall only samples, we also analyzed fall-only DOC trends, and found that trend significance did not change. Trendlines were created using LOESS (locally weighted smoothing); HVR and VWHT were graphed using LOESS.

DOC and physical lake properties (Table 2.1.) were approximately normally distributed, so data were not transformed. The relationship between percent change of HVR, DOC concentration, DOC quality (FI, SUVA, HIX, and freshness), and physical lake parameters (volume, elevation, percent slope, surface depth, maximum depth, watershed ratio, and wetland size) were assessed using multivariate linear regression. Due to a relatively small sample size, we were unable to utilize larger multivariate models or stepwise regression selection techniques. Collinearity with DOC concentration was evaluated using the variance inflation factor (VIF), using 10 as a threshold, and all available physical lake parameters that were not collinear with DOC were used (Doetterl et al., 2015). An interaction term in the model assessed the interaction between DOC and physical lake parameters. The relationship between HVR and mean Schmidt stability was analyzed using simple linear regression. Mean Schmidt stability was log transformed to remedy skewed data.

Results

DOC concentrations between 5–30 mg/L categorize Newbert, Bean, Bracey, and Jellison as intermediate DOC lakes. Salmon, Crystal, and Little Long are low DOC lakes with concentrations <5 mg/L (Figure 2.2.) (Kahl, 1998). All lakes except Crystal had higher DOC concentrations in the epilimnion than the hypolimnion, and this is consistent with trends from previous years (Appendix Figure 1). SUVA ranged from 0.6 to 4.7 and was consistently higher in the hypolimnion than the epilimnion, except for Bean and Newbert. SUVA was highest in Jellison (4.7), and lowest in Newbert (0.6). FI ranged from 1.3 to 1.6, was consistently higher in the hypolimnion than the epilimnion, and was highest in Crystal (1.6) and lowest in Newbert (1.3 (Figure 2.2.).

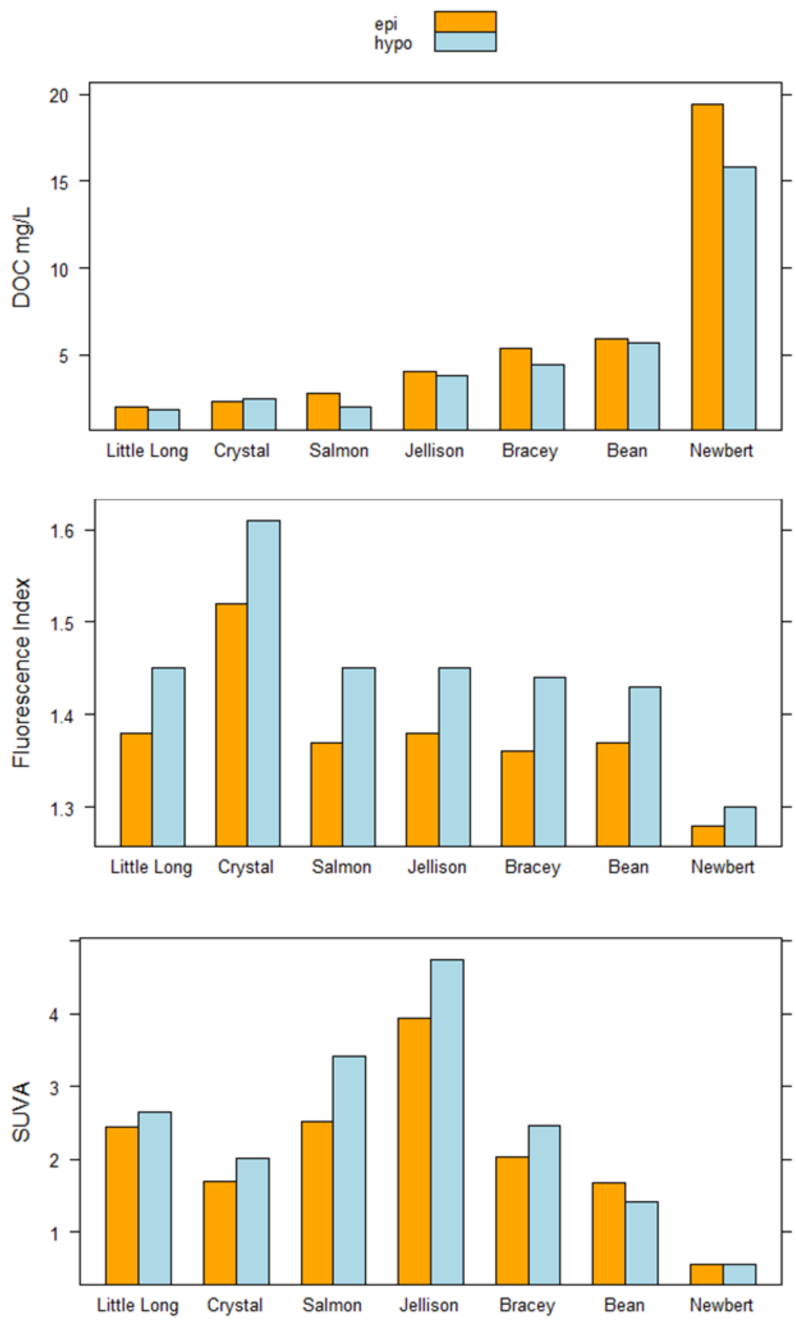

Figure 2.2. DOC quantity and quality metrics for eight lakes in Maine that were used in this study.

Epilimnion values are in orange, and hypolimnion values are in blue.

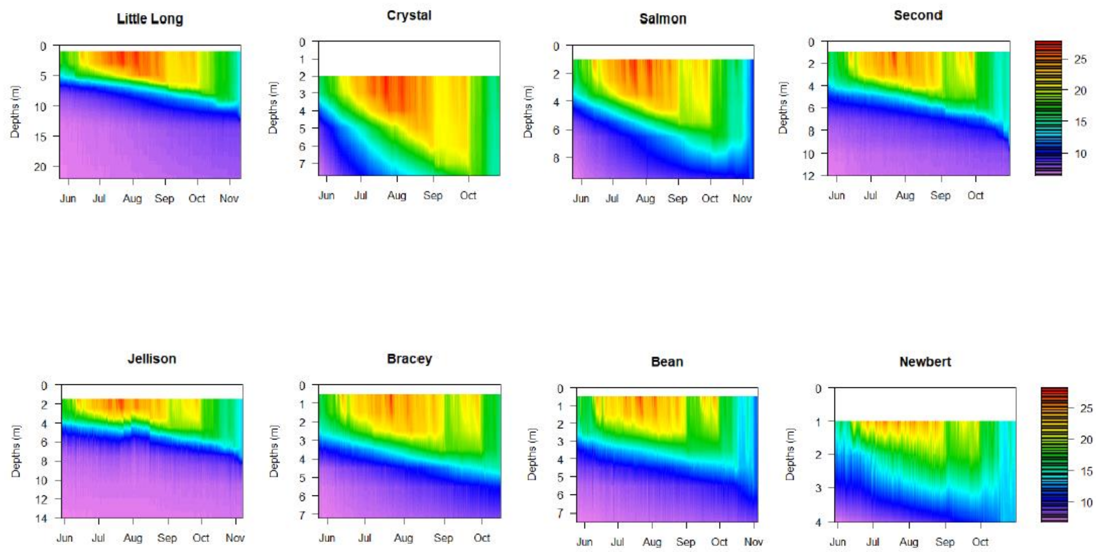

Figure 2.3. Temperature profiles from June 1, 2018 to early November for eight Regional Long-Term Monitoring-Temperature lakes in Maine that were used in this study. Depth axis differs for each lake.

Lake	HVR Rate of Change, m^3/day	HVR Percent Change, %	Total Volume loss, m3
Newbert	-0.0029	100	64786
Crystal	-0.0028	100	24663
Salmon	-0.0023	100	4716
Bracey	-0.0015	31	14319
Second	-0.0013	35	19955
Little Long	-0.0012	35	29414
Bean	-0.0007	60	11951
Jellison	-0.0006	12	8995

Table 2. 2. Hypolimnia change metrics for eight Regional Long-Term Monitoring-Temperature lakes in Maine that were used in this study.

The HVR decreased in all lakes over the course of summer stratification. Median HVR at the onset of temperature monitoring on June 1, 2017 (ordinal day 152) was 0.37 and decreased to a median of 0.14 on September 1, 2017 (ordinal day 244) (Figure 2.4.). Overall, the intermediate DOC lakes (DOC>5 mg/L) had relatively larger initial HVRs, except for Bean. Average HVR decreased over the course of summer stratification for all lakes and was 0.001 m^3/day. Crystal and Salmon had the greatest decreases in HVR, at 0.0028 and 0.0023 m^3/day, respectively (Table 2.2.). Bracey, Second, Newbert, and Little Long all had similar rates of change, ranging between 0.0015 and 0.0012 m^3/day. Bean and Jellison had the least amount of change in HVR, below 0.0007 m^3/day. Three lakes, Crystal, Salmon and Newbert, had hypolimnia that disappeared by the end of the summer stratification period (Figure 2.3. and Figure 2.4.). Interestingly, Jellison had the largest initial HVR and the smallest change in HVR over the course of the summer, yet Bean had the lowest initial HVR and second smallest change in HVR over the course of the summer. Newbert had the second largest initial HVR and the greatest total volume change in HVR over the course of the summer (Table 2.2.).

Across all lakes, average VWHT increase over the course of summer stratification was 0.02 °/day, and VWHT increased over the course of summer stratification (Figure 2.4.). Except for Crystal and Newbert, hypolimnia temperature was below 10° C in most lakes for the entirety of the summer stratification period. Jellison consistently maintained the lowest VWHT over the course of summer stratification. Crystal and Newbert both surpassed 10° C over the course of summer stratification. Crystal hypolimnion/bottom temperature heated linearly over the course of the summer at a rate of 0.07°/day, the greatest VHWT rate of change of the study set.

Both Newbert and Salmon appear to have VWHT that peak in mid-August, but this is an oversimplification from using the LOESS curve and switching between the true VWHT and bottom temperature when these lakes "loose" their hypolimnia. By examining the summer stratification

temperature profiles of both Salmon and Newbert, bottom temperatures continued to increase throughout the summer stratification period (Figure 2.3.).

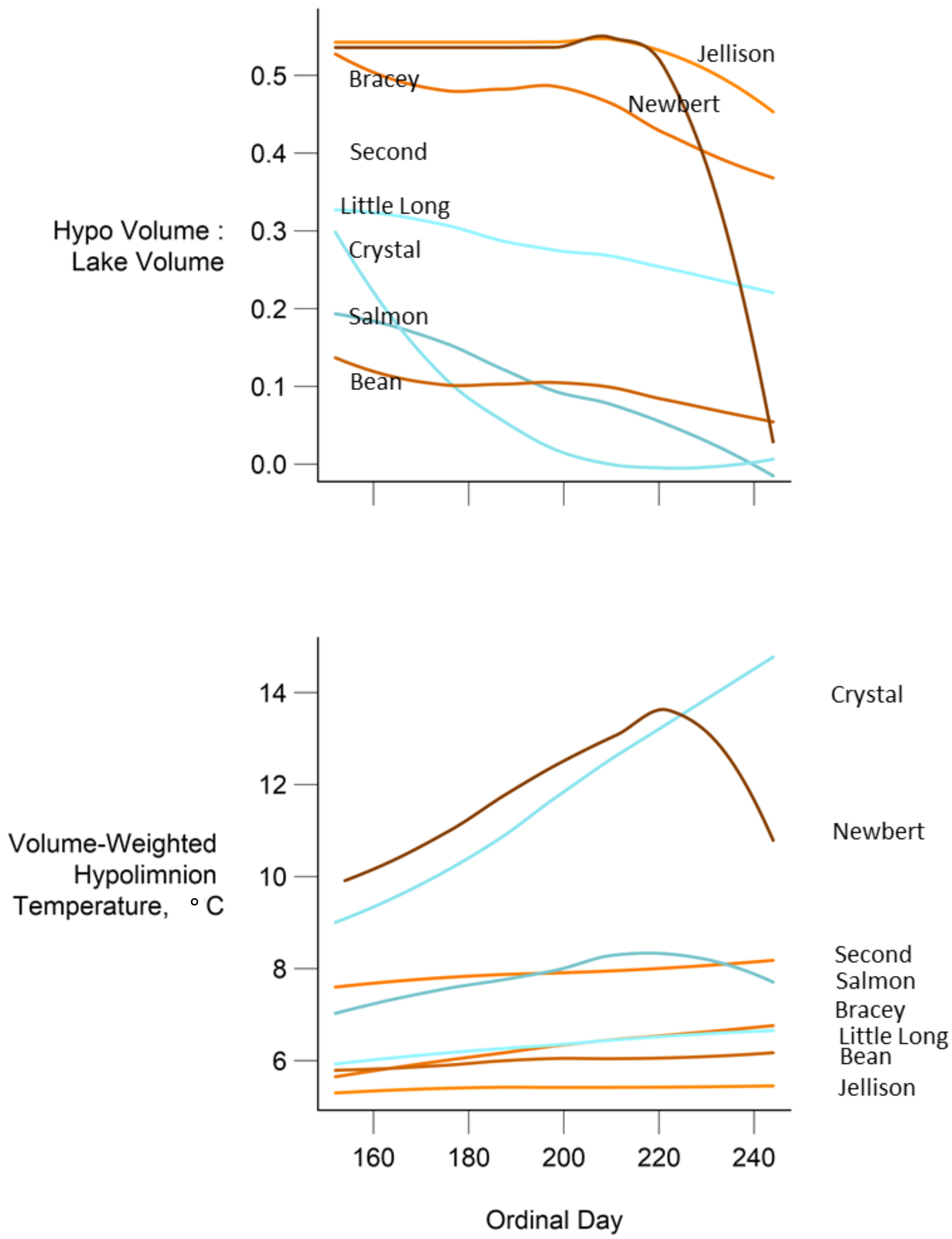

Figure 2.4. LOESS trends of a) hypolimnion volume ratio (HVR) and b) volume-weighted hypolimnion temperature (VWHT) over time. Ordinal days range from June 1, 2017 (ordinal day 152) to September 1, 2017 (ordinal day 244).

All available landscape characteristics (lake volume, elevation, surface to depth ratio, and percent slope, and maximum depth) were regressed with percent change of HVR over the course of summer stratification and interaction with DOC (Table 2.2. and Table 2.3.). Watershed to lake ratio and total wetland size are catchment parameters that were not included in multivariate models due to high VIF correlation values.

The only significant relationship with percent change of HVR was DOC concentration and the interaction of DOC concentration and maximum lake depth. The relationship between DOC concentration, maximum depth, and percent change of HVR shows that the interaction between DOC and depth, and bulk DOC concentrations were significant drivers of percent change of HVR over the period of summer stratification. This model explained 85% of the variability in percent change of HVR. The equation for this model is: Percent Change = 122.6 + 8.9 * DOC (mg/L) + 1.2 ∗ Maximum Depth (m) – 2.6 (DOC ∗ Maximum Depth) (Equation 2.1.).

When substituting indices reflective of DOM quality (i.e. FI and SUVA) in place of DOC concentrations for interaction regressions that explain the percent change of HVR throughout summer stratification, no significant relationships were found.

Mean Schmidt stability across instrumented lakes ranged from 17 to 207 J/m^2. There was a significant, inverse correlation between mean Schmidt stability and percent hypolimnion change over the course of summer stratification (p = 0.02 and r^2 = 0.61). Overall, lakes with higher mean Schmidt stability experienced less percent change in HVR over the course of summer stratification.

Multivariate Linear Regression			
Dependent Variable: Percent Change of Hypolimnion Volume: Lake Volume			
	Estimate	*p-value*	R-squared
DOC mg/L	-0.49	0.98	
Lake Volume, m^3	0.00	0.60	
DOC * Lake Volume	0.00	0.92	
			0.42
DOC mg/L	-28.38	0.31	
Elevation	-1.90	0.27	
DOC * Elevation	0.30	0.28	
			0.39
DOC mg/L	-13.62	0.41	
Surface Depth	-52.02	0.23	
DOC * Surface Depth	6.35	0.25	
			0.46
DOC mg/L	-20.29	0.41	
Percent Slope	-4.70	0.47	
DOC * Percent Slope	0.33	0.86	
			0.51
DOC mg/L	8.94	0.03	
Max Depth, m	1.22	0.52	
DOC * Max Depth	-2.60	0.02	
			0.87

Table 2.3. Multivariate, linear regressions of percent change of hypolimnion volume ratio as dependent variable with dissolved organic carbon and landscape parameters as independent variables. Significant relationships ($p \leq 0.05$) are bolded.

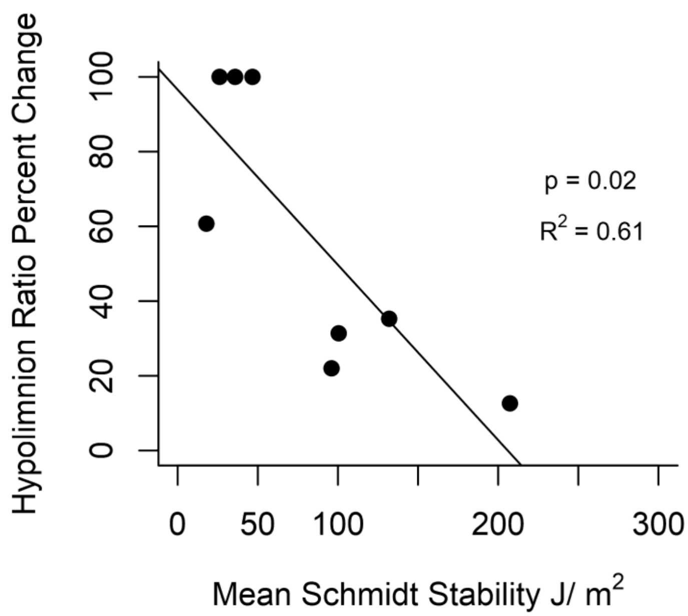

Figure 2.5. Percent change in hypolimnion volume ratio regressed with mean Schmidt stability over the course of summer stratification. Regression results used a log transformed mean Schmidt stability; however, untransformed values are shown in the figure for ease of interpretation.

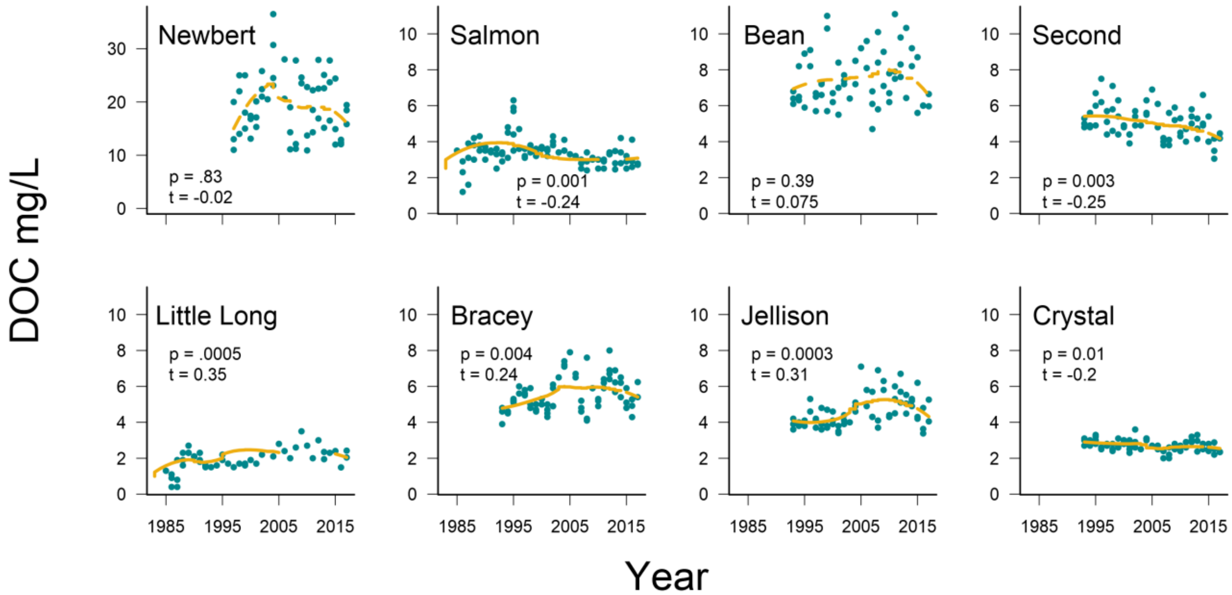

Figure 2.6. Dissolved organic carbon trends from 1985 (or onset of sampling) to summer 2017 for the eight Regional Long-Term Monitoring-Temperature lakes used in this study. Trends were analyzed with Mann-Kendall nonparametric trend test and LOESS smoothed trend lines. Solid lines are significant trends and dashed lines are nonsignificant trends ($p \leq 0.05$).

DOC concentrations across all lakes and the entire timeframe ranged from 1.2 mg/L to 36.5 mg/L, and average DOC concentration was 6.1 mg/L. When considering the time series of the entire lake population, the inception of sampling varies among lakes, but across the dataset, DOC concentrations significantly increased 0.09 mg/L per year (Figure 2.6.). For individual lakes, DOC significantly increased in three of eight RLTM-Temp lakes from the inception of a given lake's sampling history to 2017 (Bracey, Jellison, and Little Long). Three of eight lakes had significantly decreasing DOC (Crystal, Second, and Salmon), and two lakes showed no trend over time (Newbert and Bean) (Figure 2.6.).

Discussion

We hypothesized that lakes with higher DOC concentrations would exhibit a larger initial HVR and less percent change of HVR over the course of a summer stratification. Therefore, higher DOC lakes would exhibit a larger volume of cold-water refugium that is less likely to warm or disappear over the course of a summer stratification. Across eight small, north temperate lakes in Maine, we found the strongest predictors of percent change of HVR were both the interaction of DOC concentration and maximum depth and DOC concentration alone. These results suggest that bulk DOC concentrations, along with physical lake properties, do influence the availability and persistence of cold-water refugia in small, north temperate lakes and underscore the importance of understanding both chemical and physical properties of lakes in the context of environmental change.

The percent change of the HVR over the course of the summer is dependent on the interaction between maximum depth and DOC concentrations. Equation 2.1 predicts that the greatest percent change of HVR will occur in shallow lakes with relatively lower DOC concentrations followed by shallow lakes with relatively higher DOC (Table 2.3.). The smallest percent change of HVR in hypolimnion volume will occur in deep lakes with relatively higher DOC, followed by deep, low DOC lakes (Table 2.3.).

Endmembers of the depth and DOC ranges of this dataset further exemplify how hypolimnia volume changes over a summer. Despite Little Long having both the lowest 2017 summer DOC concentrations (2 mg/L) and the largest maximum depth (25m), initial HVR was greater than lakes with higher DOC concentrations, yet shallower depths (Crystal, Salmon, and Bean). Little Long percent change of HVR was lower than all lakes except Bean and Jellison. In contrast, Newbert had the highest 2017 DOC concentration (19 mg/L) and the lowest maximum depth (4 m). Despite high DOC concentrations, Newbert hypolimnion had the highest rate of HVR loss, the hypolimnion disappeared over the course of summer stratification, and bottom temperatures surpassed 10˚ C. Because Newbert is so shallow, solar

radiation was able to penetrate and accumulate in the deeper parts of the lake despite dark, DOC stained water. It has been suggested that surface depth ratio (the ratio of lake surface area to its maximum depth) is a potentially better parameter to indicate lakes that may be less resilient to high summer air temperatures and subsequent hypolimnion compression (Warren et al., 2016). Although surface depth ratio was not a significant predictor in our model, it may explain some of Newbert's vulnerability to lake bottom warming despite high DOC concentrations.

Furthermore, we can conceptualize the effects of just DOC concentrations on percent change of HVR by comparing Bracey and Crystal, two seepage lakes with similar maximum depths (9m), volumes (between 80,000 – 90,000 m^3), and relatively simple, conical bathymetries, yet different DOC concentrations (5.4 and 2.3 mg/L, respectively). Throughout the summer stratification period, Bracey maintained a larger percent volume hypolimnion and cooler VWHT than Crystal. Previous research in Canadian Shield lakes support these results, for bottom temperatures decreased with depth, yet in lakes of similar depths and bathymetries, bottom temperatures are cooler in lakes with higher DOC concentrations (Gunn et al., 2001).

When using indices reflective of DOM quality (FI and SUVA) in place of DOC concentrations for models explaining percent change in HVR, no metrics demonstrated significant relationships. This signifies that in the case of hypolimnion compression throughout the course of summer stratification, DOC quantity, not quality, is the best predictor of hypolimnion loss throughout the course of summer stratification. DOM quality characteristics such as aromaticity are known correlates with water color and depth of the photic zone, suggesting that the influence of characteristics measured by these indices, while likely relevant to HVR, are overwhelmed by other characteristics (i.e. total DOC concentration and depth) (Kothawala et al., 2014; McKnight et al.,1994; Ekström et al., 2011; Erlandsson et al., 2008; McKnight et al., 2001). For instance, Newbert Pond has both the highest concentrations of DOC and

lowest FI values in this study, which should indicate a lake rich in light attenuating DOM, preventing warming of the hypolimnion and reducing HVR. However, Newbert Pond displayed the largest absolute decrease in HVR, due to its very shallow depth of 4m. This suggests a potential hierarchy in controls on HVR with maximum depth>DOC concentration>DOC quality in these systems.

Higher SUVA values are typically associated with a greater aromatic content and in this study, SUVA was highest in Jellison (Hansen et al., 2016). Higher aromaticity is correlated with darker waters, which may explain (along with being the second deepest) why Jellison was resistant to temperature increases and HVR decreases despite not having the highest DOC concentrations. Although DOC quality metrics were not significant predictors of hypolimnion size and persistence, the changing nature of these molecules are likely influencing DOC and temperature dynamics in north temperate lakes. In a subset of coastal Maine lakes, Strock et al., 2017 found that fDOM was the strongest predictor for epilimnion thickness during summer stratification. Additionally, SanClements et al., 2012 found that FI decreased in Bracey, Jellison, and Second from 1993 to 2009, and Salmon and Crystal did not have significant changes. Long-term studies or high frequency studies that link changes in DOC quality and stratification dynamics in individual lakes over time may provide more information on how shifting molecular structure of DOC could potentially alter temperature dynamics.

Beyond maximum depth, Schmidt stability allowed us to expand beyond one-dimensional lake morphometry and consider stratification dynamics in the context of complex, individual lake bathymetry (Figure 2.1. and Figure 2.5.). Schmidt stability quantifies the strength of stratification and amount of interaction between the atmosphere and hypolimnion, and it also provides a metric to roughly quantify basin morphometry. The significant, inverse relationship between mean Schmidt stability and percent change in HVR suggests that morphometry matters; lakes with greater stratification stability and a more conical, simple basin morphometry are more likely to maintain larger hypolimnia throughout the course

of summer stratification. For example, the maximum depth of Bean (9 m) is within one meter of the RLTM temperate lakes median maximum depth (10 m), and Bean has relatively high DOC concentrations (6 mg/L). Based on our hypothesis, we expected Bean to have a larger hypolimnion and greater thermal resiliency. However, likely to do asymmetric basin morphology, in-lake islands, and shallow mean depth, Bean demonstrated relatively low stratification stability, a smaller hypolimnion volume, and less cold-water refugium. Bracey has lower DOC concentrations than Bean, and the same maximum depth, yet Bracey has a conical, symmetrical basin with a greater mean depth, likely promoting greater Schmidt stability and larger relative HVR. Although smaller lakes generally have less complex morphology, these results show that outliers with complex basin morphologies are likely to have different patterns of thermal structure than morphologically simple lakes (Sobek, 2011; L. A. Winslow et al., 2014).

Although all lakes in the Northeast have been exposed to some degree of atmospheric deposition and climate change, trends in DOC are not uniform across the region (Figure 2.6.). A lack of regional coherence suggests individual watershed and lake properties have some control on multi-decadal DOC trends (Magnuson, Benson, & Kratz, 1990). Sobek et al. (2007) have suggested DOC concentrations are regulated by a hierarchical framework that can be applied to lakes across the planet. Globally, climate and topography act as a top down driver and determine a possible range of DOC concentrations for lakes in a region (Sobek, Tranvik, Prairie, Kortelainen, & Cole, 2007). DOC concentrations in an individual lake are determined by specific watershed and lake characteristics (Sobek et al., 2007). In Maine, some lakes exhibit a coherent, predictable response to regional drivers, which suggests that anthropogenic stressors, like climate change and recovery from acidification, are driving forces of DOC dynamics (Gavin et al., 2018; Strock et al., 2017). A study in Acadia National Park, Maine, found that four of six lakes had regional coherence in Secchi disk readings from 1981 to 2008, which suggests that regional drivers were acting on physical, chemical, and biological conditions across the lake population (Strock et al., 2017). Similarly, Gavin et al., 2018 found population-wide increasing

DOC trends in 29 high elevation lakes in Maine. Given the wider geographic extent and greater landscape heterogeneity of the RLTM-Temp lake set, we would expect trends to be more variable. Lakes with static or decreasing DOC trends potentially suggest that lake-specific characteristics can modify the signal of regional drivers.

Although RLTM-Temp lakes do not demonstrate coherent shifts in DOC, multidecadal trends show both significant increases and decreases in DOC concentrations, which will likely have implications for the availability of thermal refugia in small, north temperate lakes (Figure 2.6.). For example, Crystal and Salmon are experiencing decreasing DOC trends, which suggests they may be increasingly susceptible to climate change as a result of warmer air temperatures penetrating the water column throughout summer stratification and heating the hypolimnion. Little Long demonstrated multidecadal increases in DOC concentrations, which may result in decreases in clarity. This darkening of lake water could lead to a larger hypolimnion that further buffers deep water temperatures from the effects of increased air temperature. Other lakes with increasing DOC trends may experience increases in light attenuation rate, subsequent shallower thermoclines, and larger hypolimnia (Warren et al., 2016). Only Newbert and Crystal experienced deepwater heating that would have exceeded temperatures greater than the 13 ˚C cold-water refugia threshold and cause potential harm to cold-water organisms (E. J. Snucins, Gunn, Freshwater, Unit, & Ecosystems, 1995). All other lakes maintained suitable cold-water refugium temperatures, although in Salmon and Bean, refugia size was very small.

In this study, we found that maximum lake depth and DOC are main drivers of hypolimnion persistence throughout summer stratification, where darker and deeper lakes are more likely to maintain cold-water habitat throughout the course of summer stratification. The higher thermal stability in deeper, darker lakes restricts hypolimnion exchange with the atmosphere, which essentially shields deeper waters from increasing temperatures driven by air temperatures. This suggests that deeper and

darker lakes may be more resilient to climate change than lakes with static or decreasing DOC. A growing body of evidence suggests that clear lakes are most sensitive to climate change, and this study can expand that finding and suggest that thermal refugia are more likely to be depleted in shallower, clear lakes, than deep, clear lakes which can retain cooler, larger hypolimnia (Snucins and Gunn, 2000; Gunn et al., 2001; Read and Rose, 2013; Warren et al., 2016; Richardson et al., 2017; Strock et al., 2017). Linking lake physical properties with biogeochemical trends treats lakes as integrated systems and supports a more complete assessment of how lakes will respond to regional and global drivers of change.

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THESIS APPENDIX

Text 1: Laboratory Quality Assurance Information

HELM lake samples were collected and analyzed by the same laboratories and PI team as other LTM program components; though projects originated under separate funding, they were all developed by the same founding PIs at the University of Maine (Kahl) and US EPA (Stoddard). Due to changes in PI institutions, samples in different time periods have been analyzed at different laboratories. Throughout all lab changes, the same Quality Assurance Project Plan (QAPP) was used. The original laboratory for sample analysis was the University of Maine Environmental Chemistry Lab (later renamed Mitchell Center Lab, and Sawyer Lab). Sample analysis transferred from UMaine to Plymouth State University (PSU) with PI Kahl in 2006: the PSU laboratory was set up under supervision of Kahl and with staff who oversaw analyses at UMaine, using the same instrumentation, SOPs, standards, and QC/QA procedures. When sample analysis transitioned from PSU to UNH in 2010, the laboratory manager from PSU moved to UNH with the project, used the same analytical methods and SOPs, and as with previous transfers, the QAPP was kept consistent. Measures of acidity (ANC, EqpH, ClpH) were conducted on exact instrumentation that transitioned from PSU to UNH. Major ion components were conducted on instrumentation from the same company (Dionex) at UMaine, PSU, and UNH.

The same source for Certified Reference Materials was used across the multiple labs and analyzed for anions, cations, DOC, TDN, Si, TP, Al, and pH. Any samples analyzed on a run that was outside the recovery limits for the CRM was re-analyzed. Conductivity and ANC were compared with lab made checks. In addition, all labs throughout the project period participated in the Environmental Canada Laboratory Proficiency Testing Program to ensure compliance with all lab measurements. One single EPA approved QAPP (with periodic revisions) was used across UNH, PSU, and UMaine laboratories. UMaine PI S.J. Nelson has been running QA and conferring with founding PI J.S. Kahl since 2000, for 3 data beginning in the 1999 sampling season. Prior to Nelson, two lab technicians at the

UMaine laboratory performed QA under supervision of Kahl, or QA was performed by Kahl for the earliest project years. All QA for all project years used SAS routines developed by founding PI Kahl based on EPA procedures used in ELS-I and EMAP.

Table A. 1: Mean temperature in degrees C averaged across Maine's high elevation lake region using Parameter-elevation Regressions on Independent Slopes Model (PRSIM) at 4km. PRISM data was generated using Climate Reanalyzer [*Climate Reanalyzer*, 2016].

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Parameter-elevation Regressions on Independent Slopes Model (PRISM) at 4km																	
Temperature at 2 meters (deg C)																	
Values averaged across Region (44.6N-45.6N;288.6E-291.9E)																	
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This file was generated by Climate Reanalyzer (http://cci-reanalyzer.org)																	
Climate Change Institute; University of Maine; USA (http://climatechange.umaine.edu)																	
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Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ann	DJF	MAM	JJA	SON
1980	-9.02	-10.09	-4.19	4.42	10.19	14.18	18.1	18.14	11.41	4.93	-1.19	-11.49	4.28	-8.21	3.47	16.81	5.05
1981	-14.39	-3.46	-1.7	4.61	11.53	15.92	18.51	16.96	12.14	5.34	0.67	-4.96	4.56	-9.78	4.82	17.13	6.05
1982	-15.36	-10.17	-4.38	2.04	10.93	14.1	18.34	15.48	13.26	6.95	2.03	-3.81	4.02	-10.17	2.87	15.97	7.41
1983	-8.57	-7.18	-1.16	4.32	9.1	16.4	18.83	17.84	14.3	6.81	1.16	-7.84	5.67	-6.52	4.09	17.69	7.42
1984	-11.89	-4	-6.67	4.28	9.45	15.49	18.75	18.98	11.33	7.56	0.77	-5.13	4.69	-7.91	2.35	17.74	6.56
1985	-13.2	-7.82	-3.67	3.05	10.07	14.01	18.72	16.48	13.11	6.96	-0.15	-9.67	4.37	-8.72	3.15	16.4	6.64
1986	-9.33	-9.73	-3.13	6.27	11.1	14.04	17.04	16.49	11.04	6.15	-1.62	-6.48	4.05	-9.58	4.74	15.86	5.19
1987	-10.92	-9.86	-1.91	6.12	10.61	16.05	18.48	16.4	12.54	6.49	-0.65	-5.31	4.74	-9.09	4.94	16.97	6.13
1988	-10.99	-8.83	-3.95	3.99	11.56	15.09	19.66	18.54	12.01	4.87	1.42	-9.02	4.84	-8.38	3.86	17.76	6.1
1989	-9.09	-9.96	-5.68	2.02	12.09	15.73	18.05	16.72	12.82	7.07	-1.24	-15.67	4.13	-9.36	2.81	16.83	6.22
1990	-5.98	-8.88	-3.07	3.91	9.13	15.87	18.51	18.59	12.55	8.07	1.01	-4.31	4.5	-10.18	3.33	17.66	7.21
1991	-11.32	-7.29	-2.16	4.63	11.85	16.08	18.11	18.25	11.39	7.42	0.91	-8.16	5.3	-7.64	4.77	17.48	6.57
1992	-10.68	-9.14	-5.66	2.04	10.29	15.33	15.91	16.95	12.95	4.97	-0.75	-5.73	3.67	-9.33	2.22	16.07	5.72
1993	-9.33	-14.64	-4.86	3.98	10.75	15.31	18.36	18.55	12.59	4.34	0.1	-6.05	4.12	-9.9	3.29	17.41	5.67
1994	-15.89	-12.21	-3.61	3.17	9	17.29	20.12	16.81	12.28	7.23	2.02	-4.82	4.18	-11.38	2.85	18.08	7.17
1995	-7.1	-11.19	-2.29	1.51	9.65	16.95	19.59	18.01	10.94	9.03	-1.22	-8.79	4.92	-7.7	2.95	18.18	6.25
1996	-10.79	-9.19	-4.37	3.38	8.91	16.03	17.58	17.69	13.32	5.85	-1.2	-2.56	4.04	-9.59	2.64	17.1	5.99
1997	-10.55	-7.78	-5.39	2.31	7.82	16.06	18.48	16.98	12.49	6.01	-0.77	-6.38	4.42	-6.96	1.58	17.17	5.91
1998	-8.34	-5.16	-1.91	4.72	13.32	15.07	18.56	17.92	13.53	6.88	0.78	-3.11	5.75	-6.62	5.38	17.18	7.06
1999	-10.33	-6.67	-1.54	4.09	12.52	18.13	19.73	17.4	16.17	5.41	2.66	-4.25	6.21	-6.7	5.02	18.42	8.08
2000	-10.86	-8.6	-0.45	3.45	9.46	15.07	16.89	16.96	12.31	6.66	1.37	-8.73	4.84	-7.9	4.16	16.31	6.78
2001	-10.72	-9.86	-5.17	2.79	11.88	17.13	17.59	19.21	14	7.96	2.55	-2.29	4.89	-9.77	3.17	17.98	8.17
2002	-6.16	-6.97	-3.29	4.07	9.07	14.53	18.44	19.16	15	5.07	-0.96	-6.49	5.47	-5.14	3.28	17.38	6.37
2003	-13.08	-11.47	-4.72	2.05	9.67	16.13	18.82	19.02	14.47	6.71	1.53	-5.62	4.39	-10.35	2.33	17.99	7.57
2004	-14.67	-8.72	-2.03	3.85	11.01	14.16	17.91	17.95	13.53	7.18	0.56	-7.36	4.59	-9.67	4.27	16.67	7.09
2005	-11.75	-7.86	-4.95	4.71	8.05	17.55	19.35	18.47	14.95	8.16	1.41	-6.18	5.06	-8.99	2.6	18.46	8.17
2006	-5.62	-7.5	-2.48	5.14	11.44	17.31	20.39	16.2	13.16	6.77	3.51	-2.41	6.01	-6.43	4.7	17.97	7.81
2007	-8.68	-12.65	-4.26	2.25	10.43	16.15	17.57	17.25	13.9	9.41	-0.69	-8.08	4.86	-7.91	2.81	16.99	7.54
2008	-7.9	-8.24	-5.32	4.86	9.8	16.41	19.64	16.94	13.37	6.2	0.98	-7.09	4.89	-8.07	3.11	17.66	6.85
2009	-14.09	-8.28	-3.81	5.33	10.36	14.53	16.98	18.52	12.51	4.83	3.04	-6.01	4.4	-9.82	3.96	16.68	6.79
2010	-7.21	-4.9	1.06	6.91	12.47	15.7	20.64	18.33	14.54	6.82	1.11	-5.61	6.62	-6.04	6.81	18.22	7.49
2011	-9.72	-9.44	-3.39	3.64	11.5	15.63	19.66	18.13	15.08	8.27	3.57	-3.71	5.61	-8.26	3.91	17.81	8.97
2012	-8	-6.24	0.55	5.48	12.28	15.62	19.76	19.59	13.25	8.81	0.21	-4.51	6.47	-5.98	6.11	18.33	7.42
2013	-9.51	-7.07	-1.67	3.46	11.25	16.29	20.24	17.8	13.87	8.68	0.02	-8.51	5.74	-7.03	4.35	18.11	7.52
2014	-10.7	-9.76	-8.64	3.48	10.95	16.19	19.49	17.84	13.64	9	-0.38	-3.65	4.79	-9.65	1.93	17.84	7.42
2015	-12.01	-15.74	-6.64	2.89	13.49	14.11	18.28	19.26	16.59	6.01	2.47	-0.88	4.82	-10.46	3.24	17.22	8.36

Table A.2 : Total precipitation in mm averaged across Maine's high elevation lake region using Parameter-elevation Regressions on Independent Slopes Model (PRSIM) at 4km. PRISM data was generated using Climate Reanalyzer [*Climate Reanalyzer*, 2016].

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Parameter-elevation Regressions on Independent Slopes Model (PRISM) at 4km																	
Total Precipitation (mm)																	
Values averaged across Region (44N-46N;289E-292E)																	

This file was generated by Climate Reanalyzer (http://cci-reanalyzer.org)																	
Climate Change Institute; University of Maine; USA (http://climatechange.umaine.edu)																	
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Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ann	DJF	MAM	JJA	SON
1980	31.17	24.9	98.15	121.72	35.11	69.7	127.26	63.5	120.8	105.16	107.67	50.8	970.68	121.64	254.98	260.45	333.62
1981	30.65	96.58	31.16	85.57	89.92	110.85	129.84	103.46	174.62	155.74	78.36	122.55	1137.53	178.03	206.64	344.14	408.72
1982	96.79	69.97	73.11	95.28	31.59	123.65	59.46	98.84	79.3	35.17	129.47	49.28	1015.17	289.31	199.97	281.95	243.95
1983	90.97	74.81	145.86	211.71	146.27	46.83	111.89	96.3	61.36	71.58	255.62	169.23	1362.48	215.06	503.84	255.02	388.57
1984	50.6	111.76	135.53	82.38	189.82	164.47	90.56	53.53	39.58	62.55	66.84	83.74	1216.87	331.59	407.74	308.56	168.98
1985	26.18	78.41	74.16	40.02	74.37	99.72	82.97	107.57	93.04	69.42	119.18	54.7	948.79	188.33	188.55	290.27	281.64
1986	149	39.98	98.75	71.05	107.61	79.81	118.7	124.66	85.47	39.31	100.8	82.96	1069.83	243.67	277.41	323.17	225.58
1987	93.14	15.81	83.93	118.72	75.21	108.54	60.49	47.9	149.12	95.49	67.68	90.9	998.99	191.91	277.86	216.92	312.29
1988	54.38	74.04	36.1	82.08	60.11	61.45	120.79	150.89	41.12	102.01	167.22	34.09	1041.1	219.32	178.3	333.13	310.35
1989	44.53	56.93	69.25	87.66	199.1	112.94	50.91	133.19	107.44	79.62	131.09	47.51	1106.74	135.54	356.01	297.04	318.15
1990	103.35	58.67	49.22	95.67	143.76	123.7	88.39	113.29	85.6	204.07	104.47	148.81	1217.7	209.53	288.65	325.38	394.14
1991	72.98	29.89	131.43	98.35	96.36	72.48	57.99	213.09	115.83	106.77	92.53	67.04	1236.51	251.68	326.13	343.56	315.14
1992	103.57	77.52	109.07	52.37	20.26	108.91	90.61	95.25	67.54	80.1	89.35	43.17	961.59	248.13	181.7	294.77	236.99
1993	57.09	88.32	88.78	156.13	50.47	106.05	61.56	52.63	105.3	98.26	109.34	131.33	1017.12	188.58	295.38	220.25	312.91
1994	119.38	31.52	109.64	98.45	109.52	87.63	89.09	67.21	127.85	43.55	107.11	67.76	1122.27	282.22	317.62	243.92	278.51
1995	107.1	64.36	67.76	55.34	113.22	63.06	95.07	39.81	63.39	181.15	180.93	83	1098.95	239.21	236.32	197.94	425.48
1996	126.22	94.06	60.06	132.56	131.54	119.8	186.88	36.85	138.19	95.05	48.69	162.58	1252.89	303.28	324.16	343.53	281.93
1997	105.92	59.47	88.25	87.41	96.11	88.91	91.9	119.23	82.21	34.65	116.08	66.02	1132.72	327.96	271.77	300.04	232.94
1998	149.62	98.68	106.8	87.54	91.37	211.55	95.16	61.4	63.04	145.94	71.78	46.05	1248.9	314.33	285.71	368.11	280.76
1999	153.13	63.23	157.63	17.7	78.16	89.54	72.64	76.66	239.24	117.02	92.99	74.14	1203.99	262.41	253.49	238.84	449.25
2000	95.89	79.71	100.19	155.76	119.84	67.29	107.07	60.07	64.23	94.73	79.91	120.86	1098.84	249.74	375.79	234.43	238.87
2001	35.01	75.67	107.82	24.02	50.28	98.84	86.69	36.37	94.96	43.77	60.34	63.19	834.64	231.55	182.12	221.9	199.07
2002	73.45	88.64	96.49	126.17	86.79	111.55	87.74	24.66	113.34	83.97	115.59	82.95	1071.58	225.28	309.45	223.95	312.9
2003	36.5	64.51	91.72	48.95	87.71	81.96	78.12	83.31	124.91	217.6	116.85	169.35	1115.09	183.96	228.38	243.39	459.36
2004	19.72	42.67	39.41	94.59	103.03	56.06	119.46	161.29	62.07	60.07	113.74	107.87	1041.44	231.73	237.03	336.81	235.87
2005	61.35	65.63	106.47	201.51	159.16	88	97.01	103.12	111.63	306.37	165.17	129.97	1573.27	234.84	467.13	288.13	583.16
2006	108.23	65.27	30.94	60.97	147.82	197.61	140.43	106.55	71.52	204.06	127.51	79.35	1390.88	303.47	239.73	444.59	403.1
2007	68.63	52.61	100.32	179.06	87.61	70.96	81.73	103.4	57.58	129.32	176.63	115.17	1187.21	200.59	367	256.09	363.54
2008	65.4	140.14	113.04	110.91	37.51	148.38	133.77	120.76	161.84	101.12	157.19	125.6	1405.23	320.71	261.46	402.91	420.15
2009	64	68.01	61.01	105.35	104.81	183.52	169.69	100.1	44.75	143.29	132.26	112.09	1302.39	257.62	271.16	453.31	320.3
2010	84.77	80.92	139.24	71.56	46.65	143.94	68.73	72.03	142	151.93	139.55	164.27	1253.41	277.77	257.45	284.71	433.48
2011	53.4	82	115.26	133.9	134.32	84.58	66.63	184.14	99.97	126.59	64.22	83.72	1309.29	299.67	383.48	335.35	290.78
2012	79.58	39.88	50.78	107.79	133.08	199.15	46.98	118.76	119.72	188.89	31.57	142.94	1199.92	203.19	291.65	364.89	340.19
2013	27.86	80.1	64.36	50.76	146.65	164.89	117.18	111.65	154.69	32.99	112.97	104.16	1207.03	250.89	261.77	393.72	300.65
2014	93.59	79.47	107.1	85.39	114.54	122.68	167.95	91.07	38.02	178.09	92.55	161.22	1331.65	277.22	307.02	381.69	308.66
2015	86.18	46.14	43.16	83.51	68.18	159.21	81.55	102.16	93.85	162.81	59.88	138.02	1124.66	293.54	194.86	342.91	316.54

Table A. 3: Results of linear regressions for coefficient of variation of the DOC concentrations in the 29 lakes in a given year as a function of temperature in ˚C and time.

Mean Temperature	Estimate	*p*- value	r^2
November	-0.008	0.456	0.035
December	-0.011	0.162	0.118
January	-0.002	0.814	0.004
February	-0.007	0.312	0.064
March	-0.005	0.418	0.041
April	0.011	0.408	0.043
May	-0.005	0.605	0.017
June	-0.012	0.423	0.041
July	-0.022	0.100	0.160
August	-0.024	0.140	0.126
September	-0.029	0.005	0.401
October	0.000	0.985	0.000
March - September	-0.036	0.069	0.193
May - September	-0.042	0.023	0.285
Year	-0.004	0.034	0.252

BIOGRAPHY OF THE AUTHOR

Amanda Leigh Gavin was born in Newburyport, Massachusetts on May 7, 1990. She was raised on the Northshore of Massachusetts and graduated from Pentucket Regional High School in 2008. She attended University of Vermont and graduated in 2011 with a Bachelor of Science degree in Plant Biology. After graduation, Amanda moved to Oregon and began working as a riparian Botanist for PacFish/InFish Biological Opinion Monitoring Program (PIBO), a fish habitat monitoring project with the US Forest Service. She continued working for this project for four years, surveying remote headwater streams in Montana, Idaho, Washington, Oregon, Nevada, and Utah. In the off-seasons, she taught environmental education on Orcas Island, Washington and was a ski patroller in Montana. In 2016, Amanda worked for MPG Ranch as an upland, range, and forest botanist before moving to Maine to start her Master of Science degree. The first chapter of this thesis, Acidification and climate linkages to dissolved organic carbon in high elevation lakes was accepted by Water Resources Research in May 2018 (DOI: 10.1029/2017WR020963). Upon completion of her Master of Science degree, Amanda will be working in Portland, Maine for FB Environmental as a Project Scientist. Amanda is a candidate for the Master of Science degree in Ecology and Environmental Sciences from the University of Maine in August 2018.