LONG-TERM PATTERNS OF DISSOLVED ORGANIC CARBON IN BOREAL LAKES

A Thesis

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By

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ABSTRACT

I analyzed the 21 year dynamics of dissolved organic carbon (DOC) in 55 lakes in five sites across Eastern Canada in relation to regional and global variables. Regional variables included total solar radiation (TSR), precipitation (PPTN), air temperature (T) and sulfate deposition (SO_4). Global variables included the Southern Oscillation Index (SOI), North Atlantic Oscillation (NAO) and Pacific Decadal Oscillation (PDO). A synchronous pattern in DOC was found among lakes within each region; however, a synchronous pattern in DOC was not found between sites, except for Kejimkujik and Yarmouth which were only 80 km apart from each other. This suggested that the variation of the long-term DOC pattern was in response to the temporal pattern of regional variables, and it supports the recent understanding that regional factors have a strong influence on many lake properties. Significant long-term trends in DOC were not evident except at the Experimental Lakes Area (ELA), where an increase in DOC was observed together with a decrease in summer TSR and an increase in summer precipitation. Annual mean air temperature has increased at the Nova Scotia and Turkey lakes sites over the study period.

The relationship between the long-term pattern in DOC with the regional and global variables was analyzed for each study site to determine the key variables that could best explain the variation in the long-term pattern in DOC. TSR and PPTN were important independent variables across all sites, except for the Turkey Lakes Watershed site (TLW). Summer TSR (annual TSR for Kejimkujik and Yarmouth) had a negative relationship, while summer precipitation had a positive relationship with the long-term DOC pattern for all sites except TLW. TSR and PPTN explained 78%, 49% and 84% of

the variation in the long-term DOC pattern at Dorset, ELA, and Nova Scotia (NS) sites, respectively. In contrast, the long-term pattern in DOC at TLW only had a weak relationship with the regional and global variables considered.

A General model was developed to compare the strength of the response of DOC to the regional variables among sites. Therefore, only the variables which had a significant linear correlation with DOC across sites were selected. If a site had no variables in common with other sites, it was excluded from the general model. This resulted in TLW being excluded from the general model because the long-term DOC pattern at TLW was not significantly correlated with any regional variables.

The best general model included TSR from Dorset, ELA and NS sites and precipitation from only the NS site. The strengths of the response of DOC to precipitation were weak at Dorset and ELA compared to NS, therefore, they were excluded. The general model explained 91% of the site-to-site variation of DOC among sites. Among them, TSR was an important negative variable which contributed 56% of the explanation to the general model. Precipitation at NS was an important positive variable for the general model. It contributed 34% of the explanation to the model. As the response of the long-term DOC pattern to the changes of environmental variables (TSR and PPTN) was very strong at NS, the NS site dominated the general model, and its temporal (year-to-year) variation in the long-term DOC pattern explained 60% of the site-to-site variation of DOC in Eastern Canada. The other two sites, Dorset and ELA, had weak contributions (20% and 11%, respectively) to the general model.

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CHAPTER 1. INTRODUCTION

1.1. The nature of Dissolved Organic Carbon (DOC)

Carbon can be classified as inorganic carbon (e.g., CO, CO_2, H_2CO_3) and organic carbon, the latter includes both living and non-living organisms. Biological processes convert organic and inorganic carbon into one another. For example, photosynthesis converts inorganic carbon into organic carbon and respiration converts organic carbon into inorganic carbon. Organic carbon includes non-living biomass (e.g., excretory and secretory compounds) and dead organisms. It can be further divided into particulate organic carbon (POC) and dissolved organic carbon (DOC) based on size. DOC is defined as the fraction of the organic carbon in water that passes through a 0.45 or 0.2 μm pore size filter (Thurman, 1985).

1.1.1. Sources of DOC

DOC is found in both aquatic and terrestrial systems. DOC in aquatic systems can originate from various sources (e.g. in-lake processes, terrestrial processes, and from exchanges between air and water). However, it originates mainly from two sources: in-lake processes and from the surrounding terrestrial systems (Lennon, 2004; Aitkenhead-Peterson et al., 2003; Bertilsson and Jones, 2003). The fraction of DOC that is created from in-lake processes is classified as internal or autochthonous DOC, and DOC derived from sources outside of an aquatic ecosystem is defined as allochthonous DOC (Wetzel, 2001; Reche & Pace, 2002).

Autochthonous DOC is derived mainly from indigenous primary production (e.g., algae and macrophytes) (Wetzel, 2002). The term, P-DOC, will be used here to represent this type of photosynthetically produced DOC. P-DOC primarily consists of monomeric compounds, aliphatic carbon and some algal-derived fulvic acids. Therefore, its chemical structure can easily be defined as soluble fats, proteins, carbohydrates and organic acids (e.g. carboxylic acids). P-DOC lacks colored compounds; therefore, it is usually not pigmented and does not influence the color of a lake. P-DOC can be characterized by its low capacity to absorb light (Morris 1981; Tipping et al. 1988; McKnight et al. 1994, 1997; Sun et al. 1997, Reche & Pace, 2002). Since P-DOC is more recent, labile, and has a lower molecular weight than allochthonous DOC (Morris, 1981; Bertilsson and Jones 2003; Sinsabaugh and Findlay, 2003), it is preferentially utilized by bacteria over DOC from terrestrial systems (Jensen, 1983, Baines, 1991). Approximately 34 to 90% of the P-DOC was found to be rapidly used by bacteria (Jensen, 1983; Sondergraard et al., 1985).

Previous studies have observed that P-DOC was about 5-20% (Mulholland, 1992; Kaplan and Bott, 1982) of the total DOC in streams (Kritzberg et al. 2004). However in a special case, over 90% of the total DOC observed in lakes, streams and a wetland was P-DOC (Bertilsson and Jones, 2003), and it increased with algal spring blooms. P-DOC is not directly related to climatic regional variables (e.g., temperature, solar radiation and precipitation); however, climatic variables do influence it indirectly through the growth of aquatic biota (Aitkenhead-Peterson et al., 2003).

Allochthonous DOC, in contrast, is derived from sources outside of aquatic ecosystems (e.g., terrestrial systems). This type of DOC is derived from non-living terrestrial plant matter or humic substances (e.g., cellulose, lignin, tannins) through both microbial and abiotic processes, (e.g. decomposition and photo-degradation of terrestrial plant biomass) (Reche & Pace, 2002). Furthermore, allochthonous DOC is extensively processed as it passes through soil before entering aquatic systems (Wetzel, 2001b; Hasland, 1998). This results in the production of humic components and colored polymers (such as natural acids and chromophores) with large molecular weights in most lakes. Therefore, allochthonous DOC is a complex mixture that is usually referred to as humic substances (HS) or colored DOC (C-DOC) as it enters lakes. These naturally occurring humic compounds are difficult to identify because they usually associate with multiple double bonds in aromatic, aldehyde and ketone groups (Wetzel, 2001; Osburn and Morris 2003; Leenheer and Croue, 2003). HS are expected to have hydrophobic components and are relatively recalcitrant to further decomposition (Schiff et al., 1997); they are less susceptible to biological utilization than substrates originating from algal production (nonhumic substance) (Wetzel, 2001; Kritzberg, 2004).

HS include fulvic acids and humic acids (Wetzel, 2001; Mcknight and Aiken, 1998; Osburn and Morris 2003). The molecular weights of fulvic acids vary from 500 daltons (D) to 1200 D (Peuravuori and Pihlaja, 1999), while humic acids vary from 1200 to 5000 D (Cabaniss et al., 2000). The lower molecular weight fractions of HS are more hydrophilic, mobile and bioavailable. In contrast, HS with higher molecular weights contain more hydrophobic organic compounds, greater aromatic structures, decreased mobility and are less susceptible to biological utilization (Mcknight and

Aiken, 1998; Wetzel, 2001 and 2003). Fulvic acids account for approximatly 40-60% of the DOC of many aquatic systems (McKnight and Aiken, 1998; Malcolm, 1990). Fulvic acids contain many acidic functional groups (e.g., carboxyls, hydroxyls and carbonyls, and primary carboxylic acids) (McKnight and Aiken, 1998); they are highly oxidized, stable and water soluble (Schnitzer, 1971). As described by Wetzel (2001), fulvic acid is a naturally occurring metal complexing agent that can bring di- and trivalent metal ions into stable solution from practically insoluble hydroxides and oxides. The carboxylic acid groups are of major importance in natural organic matter because they dominate the acidity and contribute to the solubility of the fulvic compounds.

Humic acids, or high molecular weight HS, are usually present in a colloidal structure, which provides a large surface area that is suitable for absorbing and binding inorganic and organic materials. For example, they can bind unstable metal ions into a stable solution from practically insoluble hydroxides and oxides; thus, enhancing the availability of these elements to aquatic organisms by keeping them in a dissolved state (Sunda, 1995; Wetzel, 2001; Mierle and Ingram, 1991, Perdue, 1998). Consequently, it can alter the availability of toxic metals and organic substances to aquatic biota (Wetzel, 2001; Anderson and Morel, 1978).

C-DOC is yellow to brown in color due primarily to the presence of humic acids (Osburn and Morris 2003) (Fig. 1.1). With a large capacity for absorbing light, C-DOC plays an important role in the absorption of solar radiation (Morris et al., 1995; Ferrari and Dowell, 1998; Hargreaves 2003), and therefore can alter the thermal environment of lakes (Perez-Fuentetaja et al. 1999; Snucins and Gunn 2000).

C-DOC photochemical processes: As C-DOC is exposed to solar radiation, molecules of C-DOC are electronically excited by gaining the energy from photons that elevate the outer orbital electron of atoms to a higher energy anti-bonding orbit. This can lead to photochemical reactions. These photochemical processes can modify the bonding structure of the C-DOC (Wetzl, 2001).

There are specific chemical and physical photochemical processes occurring when a C-DOC molecule absorbs solar radiation (Miller, 1998): photo-bleaching is the loss of chromophoric absorbance found in CDOC; this is also termed fading as it is associated with a loss of color. Photo-degradation is the breakdown of dissolved organic matter into smaller fractions. Photolysis is chemical bond cleavage that occurs during photo-degradation. Photo-mineralization is the oxidation of various moieties to dissolved inorganic carbon (e.g. carbon monoxide (CO) and carbon dioxide (CO_2)). Photo-oxidation is an umbrella term that includes all four of the above mentioned processes (Osburn and Morris, 2003).

When exposed to solar radiation, humic substances (CDOC) can undergo structural changes that transform large molecules into smaller molecules of DOC (e.g., small fatty acids such as acetic, formic, and citric acid) (Amon and Benner, 1996, Zepp et al. 1981). Solar radiation can also mineralize DOC with the generation of dissolved inorganic carbon (DIC) (e.g., CO_2, CO) (Miller and Zepp, 1995). The smaller molecules that result from the photo-degradation of HS have been identified in many studies (Moran and Zepp, 1997; Wetzel, 1995; Wetzel, 2000; Wetzel et al., 1995). These smaller DOC molecules are often more bioavailable to microorganisms.

1.2. The role of DOC in aquatic ecosystems

1.2.1. Effect of DOC on lake thermal properties

The absorption of solar radiation by DOC (Cooper and Lean, 1989; Maloney et al., 2005; Sun et al. 1997; Hargreaves, 2003; Williamson et al., 1999) affects aquatic ecosystems by altering the heat balance, and thus can affect the thermal stratification and the mixing depth of lakes. In turn, these properties influence the structure of biotic communities and their productivity (Perez-Fuentetaja et al., 1999; Snucins and Gunn, 2000). As the concentration of C-DOC increases, the mixing depth is expected to decrease, particularly in small lakes (Fee et al., 1996; Williamson et al., 1999). In turn, a decrease in primary productivity is also expected (Jones, 1992; Christensen, 1996; Carpenter et al., 1998; Kalff, 2001). DOC strongly attenuates ultraviolet radiation (UV) (Laurion et al., 1997; Morris et al., 1995; Williamson, 1996; Scully & Lean, 1994) and has been shown to reduce harmful UV damage to phytoplankton (Moeller 1994; Karentz et al. 1994; Molot et al., 2004; Rautio, 2002). Such as, the 1% UVB penetration depth decreased to less than 1 m from 8 m when DOC increased from 1 mg l^{-1} to 4 mg l^{-1} (Scully and Lean, 1994).

1.2.2. As a source of energy for aquatic food webs

DOC is composed of substrates that can be used by microbial food webs for energy (Hobbie, 1992; Wetzel and Ward, 1992; Wetzel et al., 1995). Most DOC derived from in-lake processes (P-DOC) can be rapidly utilized by bacteria as it consists mainly of labile, lower molecular weight compounds (Bertilesson et al., 2003). For example, up to 34 - 90 % of P-DOC was found to be metabolized by microorganisms per day (Cole

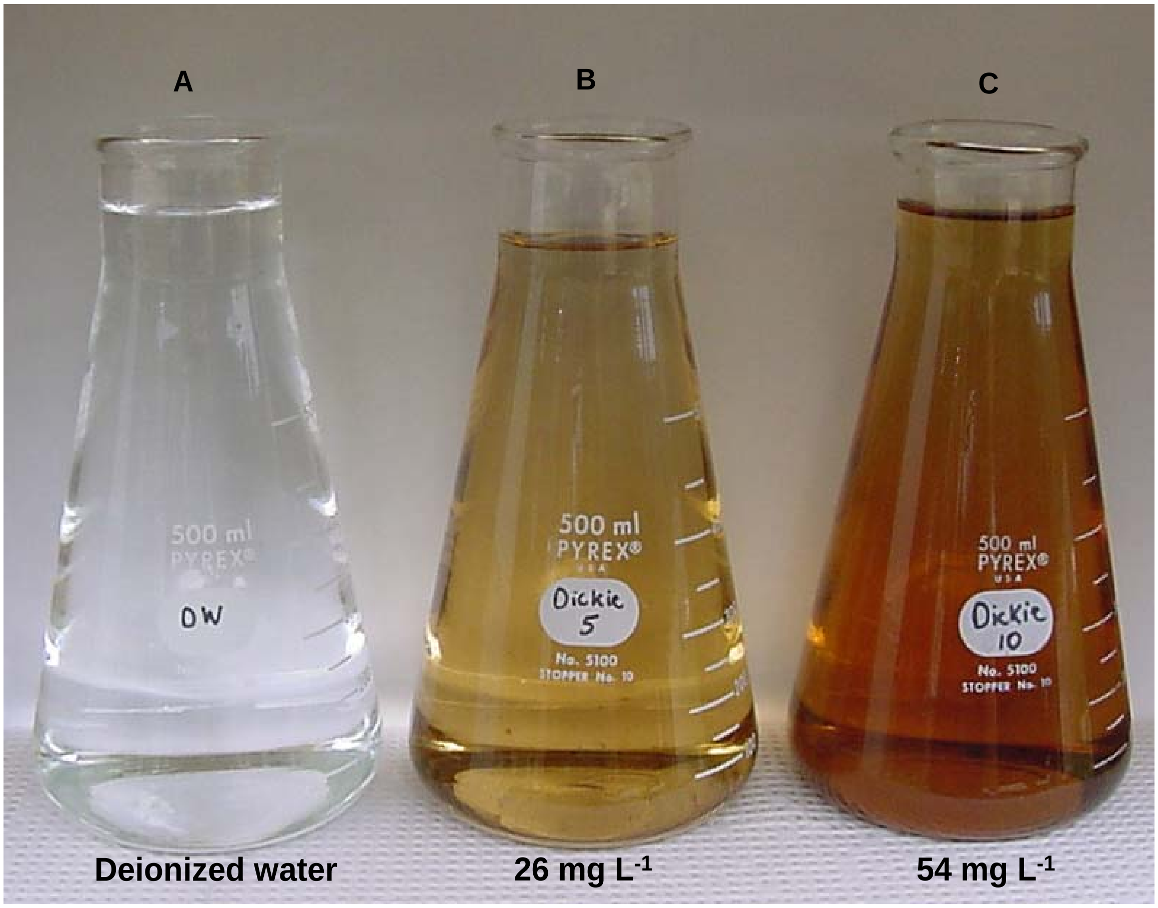


Figure 1.1. An example of dissolved organic carbon (DOC) in stream water. Two water samples (B and C) contain DOC that imparts a tea color. The water on the left (sample A) contains no DOC and is colorless (photo courtesy of Jeff Hudson).

et al., 1982; Jensen, 1983; Sondergraard et al., 1985). However, due to their large molecular structure and complicated humic acid groups, most of the DOC derived from terrestrial systems (CDOC) cannot be directly assimilated into aquatic organisms (Thurman 1985, Schiff et al., 1997, Wetzel, 2001, Kritzberg, 2004). Solar radiation, particularly ultraviolet radiation, can promote the transformation of both the structure and molecular weight of humic substances to more bio-utilizable structures and size fractions (Strome and Miller 1978; DeHaan and DeBoer 1991; Allard et al. 1994; Kulovaara et al. 1996). This can provide energy and structural carbon for biomass in aquatic food webs (Meyer and Poepperl, 2004; Kieber et al. 1989; Mopper et al., 1991) (see further information in section 1.3).

1.2.3. Toxicity and nutrient availability

DOC binds many metals and nutrients with its fulvic and humic acids, and thereby, influences the dissolved concentrations and bioavailability of metals and nutrients (Mierle and Ingram, 1991; Shaw et al., 2000; Jackson et al., 1980; Francko, 1986; Perdue 1998; Lawlor and Tipping, 2003; Wetzel, 2001). Thus, DOC can reduce the toxicity of contaminants and heavy metals (Brooks, 2007). Toxic metals impact aquatic organisms when present as free ions (Jones, 1998). The components which reduce the free ion activity, therefore, reduce the toxicity of the metals (Anderson and Morel, 1978). In many water bodies C-DOC is an important complexing agent, for example, it reduced the toxicity of copper to an estuarine diatom (Sunda and Lewis, 1978), and reduced the toxicity of aluminum and copper to fish (Burton and Allan, 1986; Witters et al., 1990; Welsh 1993). In addition, C-DOC reduced the availability of methylmercury (MeHg) to aquatic organisms (Haye et al., 2006). Humic bog water was found to detoxify zinc, lead, mercury and copper to phytoplankton assemblages (Bringolf et al., 2006; Hongve et al., 1980). On the other hand, the binding of metals by C-DOC also modifies the availability of essential metals, such as iron and anionic nutrients (e.g., phosphate) to aquatic organisms (Jones, 1998).

1.2.4. Indicator of watershed characteristics

Lake DOC, particularly allochthonous DOC, which enters aquatic systems from terrestrial systems, reflects the characteristics of the watershed. For example, DOC concentration in lakes was found to increase with an increase in the proportion of wetlands at Dorset, Ontario (Dillon and Molot 1997; Wetzel 2001), varies with different types of vegetation and land use (Frost et al. 2006; Gergel et al. 1999; Dillon and Molot, 1997; Wetzel, 2001a), watershed hydrology, and climate (e.g., precipitation) (Engstrom, 1987). Therefore, the concentration and character of the DOC reflects the properties of the watershed.

1.3 Factors that affect DOC

DOC affects the lake environment (e.g., thermal characteristics), but in turn, it is affected by specific lake characteristics (e.g., lake morphology) and environmental variables (e.g., climate). The concentration of DOC in a lake is determined by the processes that produce DOC (e.g., macrophyte growth, vegetation type, and wetlands) and processes that reduce DOC (e.g., photochemical and microbial decomposition) (Curtis 1998), as well as the quantity of precipitation falling on the landscape to transport terrestrial DOC to lakes. Therefore, the amount and quality of DOC in lakes is a combined result of in-lake processes, catchment processes, and climate.

1.3.1. Local variables and DOC

Many local variables are reported to affect DOC dynamics. The quality and quantity of DOC exported from terrestrial systems is affected by catchment characteristics (watershed properties): soil properties, hydrology (Hagedorn et al., 2000), geology (Moore T.R., 1998; Mattsson et al., 2005; Hope et al. 1994) and biological factors (Brooks et al., 1999; Lennon et al., 1987). As noted earlier, DOC loading into lakes can increase with a relative increase in the proportion of wetland in the watershed (Elder, 2000; Thurman, 1985; Dillon and Molot, 1997; Eckhardt and Moore, 1990; Hillman et al., 2004; Kortelainen, 1993). As well, spatial variation in the export of DOC among watersheds might be regulated by forest type (Agren et al., 2007), primary production (Lennon et al., 1978; Hope et al, 1994), and land use (Findlay et al., 2001; Mattsson et al., 2005; Gorham, 1998), clear-cutting, and wildfires (Carignan et al. 2000; France et al. 2000). For example, DOC concentration increased after a watershed burned in 1975 and 1980 at ELA (Schindler et al., 1996; Schindler et al., 1992). DOC is also affected by different soil types. For example, soil type can influence the carbon: phosphorus ratio in DOC (Lennon et al., 2005).

Furthermore, lake characteristics also affect DOC concentration. For example, lake acidity and Fe concentration affects the rate of DOC photodecomposition (Molot et al., 2005). Increases in the acidity and Fe concentration in a lake will accelerate photolytic processes (Molot et al., 2005).

1.3.2. Regional variables and DOC concentration

Regional variables also influence the dynamics of DOC. Total solar radiation, precipitation, temperature and sulfate deposition have been reported as key regional variables affecting lake and stream DOC concentration (Aitkenhead-Peterson et al., 2003; Bertilsson and Jones Jr, 2003; Lennon, 2004; Hudson at el., 2003; Molot at el., 2005; Futter et al. 2008). Solar radiation provides the necessary energy to break down the double bonds of DOC (Wetzl, 2001; Aarnos et al., 2007). Through photochemical processes, solar radiation (particularly UV) has been reported to cause reductions in DOC of approximately 20 – 60% over a period of 11-70 days (Andersen and Gjessing 2002; Shiller et al. 2006; Molot et al. 2005). Wetzel et al. (1995) explained the photodegradation process in detail in freshwater environments. They found that the small organic fractions, such as fatty acids, acetic, formic, citric, pyruvic acid and other fractions, generated by photolysis of humic substances, increased greatly after DOC was treated under solar radiation. They also reported that bacterial protein production was enhanced when the organic DOC substrates were exposed to ecologically relevant UV radiation (range from 240-320 nm). C-DOC was reported to lose its optical capability through photobleaching (De Lange, 2000; Reche et al., 2000), resulting in an increase of inorganic carbon production (Miller and Zepp, 1995; Wetzel, 2003) and a decrease in DOC concentration (Molot et al., 2005).

Precipitation through runoff transports terrestrial DOC from catchments to rivers and lakes. Increases in regional precipitation usually results in an increased loss of organic carbon from terrestrial systems (Clair et al. 1994; Schiff et al. 1998; Schindler et al. 1997) because DOC mass export and runoff are tightly coupled (Dillon and Molot, 2005). The effect of precipitation on lake DOC concentration is complex because catchment properties (e.g. the portion of wetland and land use, soil properties, and vegetation type) also affect the concentration of DOC (Wetzel, 2001; Bertilsson, 2003). Therefore, depending on the catchment characteristics (Dillon and Molot, 1997), season (Hudson et al., 2003), hydrological condition and the source of DOC in a lake, the relationship between precipitation and lake DOC concentration can be strong (Correll et al., 2001) or weak (Spitzy and Leenheer, 1991), positive (Reche and Pace, 2002), or negative (Sobek et al., 2007). Furthermore, the relationship between DOC concentration and precipitation can differ among sites (i.e., spatially) and from year-to-year (i.e., temporally). Most studies in a single site found that an increase in precipitation resulted in a greater export of DOC to lakes. Sobek et al. (2007) found that precipitation was an important negative variable in explaining the variation of DOC in their model, which was based on a large data set collected from North America and Europe. However, their study looked at multiple sites with only a single measurement per site; it did not consider temporal dynamics in DOC.

Many studies have suggested that global warming may indirectly influence DOC and may cause both increases and decreases in DOC concentration (Dillon and Molot 1997; Schindler et al.1997; Clair and Ehrman, 1996). Some studies reported that warming has been correlated with increases in upland DOC concentration by accelerating the decomposition processes, resulting in more DOC available for export to lakes (Freeman et al., 2001). However, temperature has been found to be unrelated to DOC concentration in lakes elsewhere (Hongve et al., 2004).

The acidification of watershed through sulfate deposition became a major international concern during the 1970's and 1980's. Since then large sulphur emission control programs have been implemented in Europe and North America with the expectation that many affected aquatic ecosystems would recover. Reductions in sulfate emissions have been correlated with increases in lake DOC (Evans, 2005). The correlation in DOC is likely a consequence of a decline in acid-enhanced photo-oxidation rates occurring via the photo-Fenton pathway (Gennings et al 2001; Molot et al. 2005). With these processes in mind, Evans et al. (2006), therefore, concluded that the reduction in SO_4 deposition was a key cause of rising DOC. Similar results were found in some lakes in North America (Driscoll et al, 2003; Bouchard, 1997). However, the decrease of SO_4 was not associated with an increase in DOC in some other sites (Clair et al, 2004, 2008; Dillon et al., 2003) because it may take many years to flush the accumulated SO_4 from watersheds. However, these studies have not considered the complex interactions between climate and lake acidity. For example, changes in precipitation and solar radiation (particularly UV) could also be responsible for such DOC dynamics (Hudson et al., 2003; Molot et al., 2005)

The Southern Oscillation Index (SOI), Pacific Decadal Oscillation (PDO), and North Atlantic Oscillation (NAO) have been used to describe global scale weather patterns. These global weather patterns might not affect DOC concentration directly but might be correlated to some local environmental conditions. For example, SOI was correlated with less precipitation in North America (Dillon, 1997).

Although many short-term and small scale experiments suggest that regional variables influence lake DOC concentration, the relationship between regional variables and DOC is complex. Many studies have explored such relationships with models that mainly consider local variables. Hanson et al. (2004) developed a model to explain the flux of lake DOC as affected by in-lake processes. Canham et al. (2004) focused on modeling the relationship between the dynamics of DOC and watershed characteristics (e.g. different vegetation coverage). Soil characteristics are another factor considered in many studies (Michalzik et al. 2003; Neff et al. 2000, Hadedorn et al. 2000). Dillon and Molot (2005) investigated the long-term trends of DOC exported from catchments. They reported that the variation in the export of DOC from catchments was affected by runoff and dry periods. These models highlight the relationship between DOC and local variables, however, the effect of local variables on DOC may also depend on regional climatic or non-climatic variables. For example, precipitation may influence the amount of DOC loading from soils into lakes, and solar radiation may affect the rate of photochemical processes that may cause reductions in lake DOC.

According to a handful of recent studies, regional variables (e.g., precipitation (PP), total solar radiation (TSR) and air temperature (T)) may be affecting long-term patterns in DOC concentrations in water bodies. Futter et al. (2007) focused on catchment properties and DOC dynamics, and emphasized that temperature and precipitation were variables which needed to be considered, but they did not include other regional variables, such as TSR. Correll et al. (2001) developed a model to predict the discharge of DOC from a river watershed. They found that DOC dynamics were correlated with precipitation and temperature. Evans et al. (2005) focused on the relationship of DOC with lake acidity and air temperature, and found that an increase in DOC was associated with a decrease in SO_4 and an increase in air temperature. Keller et al. (2005) investigated the potential effects of climate change on lake thermal structure and DOC dynamics. These studies indicate that the influence of regional variables on DOC is complex. However, these studies have only considered a limited set of regional variables at a time, and a more comprehensive approach is necessary. In particular, studies need to relate long-term patterns in DOC to the whole range of regional variables that might influence DOC, and where possible such studies should examine these relationships at multiple sites to see if they respond in similar ways. The study by Hudson et al. (2003) explored the relationship between long-term DOC patterns and regional factors at Dorset, Ontario. Of the large number of regional and global variables considered, only photosynthetically available radiation (PAR) and precipitation were found to be strongly related to the long-term pattern in DOC. Although short-term studies (e.g., days to weeks) had previously documented that solar radiation (both UV and PAR) caused reductions in DOC concentration (Gennings et al. 2001; Goldstone 2002; Molot et al. 2005), the study by Hudson et al. (2003) was the first to provide evidence that a negative long-term effect was present. However, the generality of their result to other sites is not clear and further testing is warranted.

1.4. Objectives

This project investigated whether a relationship could be identified between long-term patterns in whole lake dissolved organic carbon (DOC) and multiple regional variables at multiple sites across eastern Canada through the following steps: (1) the synchronous patterns of DOC and regional variables was examined by using temporal coherence analysis to determine how similar the variation of DOC in lakes within a site and between sites; (2) the relationships between DOC dynamics and the regional and global variables was modeled by using multiple linear regression; (3) the best regression model for each site was developed to describe the relationships between DOC dynamics and regional variables with Akaike's Information Criterion (AIC); (4) trends in DOC and regional variables for each site (linear regression) were investigated.

CHAPTER 2. STUDY SITE DESCRIPTION AND LAKE CHARACTERISTICS

2.1. Study site description

A total of 55 lakes each with over 20 years of recorded DOC concentrations were selected from Eastern Canada (Appendix 1). The study lakes were initially grouped into five sites based on geographic locations. These five sites were combined into 4 sites because two sites, Kejimkujik and Yarmouth which are in close proximity to each other, were found to have synchronous patterns in dissolved organic carbon (DOC) and regional variables (Figure 2.1; Figure 3.1). Three of the four sites were located in Ontario: Dorset (8 lakes), Turkey Lakes Watershed (5 lakes), and the Experiment Lakes Area (4 lakes). The fourth site which combined two sites (Kejimkujik with 27 lakes and Yarmouth with 11 lakes) was located in Nova Scotia.

2.1.1. Dorset

The Dorset study site is located in the boreal ecozone near the southern boundary of the Precambrian Shield, approximately 150 km northeast of Toronto. The eight lakes within this site were in the District of Muskoka and Haliburton Counties in south-central Ontario. All are individual headwater lakes. The lake catchments were primarily forested and underlain by Precambrian metamorphic plutonic and volcanic silicate bedrock. Some cottage development is found in the catchments (Dillon and Molot, 1990; Dillon and Evans, 2001). The eight lakes are oligotrophic with low DOC concentrations from 1.8 to 5.0 mg l^{-1}, 1978-1998). The surface area (Ao) of the eight lakes ranged from 21 to 94 ha (Appendix 1), and the maximum depth (Zmax) had a range of 5.8 to 38.0 m. The mean surface area to mean maximum depth ratio (Ao/Zmax) was 2.43. Dorset received a high amount of SO_4 deposition each year during the study period compared to the other sites (55.9 mEq m^{-2}) (Table 2.2).

2.1.2. Turkey Lakes Watershed (TLW)

The TLW is located in the Precambrian Shield in the Algoma District of central Ontario, approximately 60 km north of Sault Ste Marie. The TLW site is an undisturbed, completely forested basin, 1050 ha in area, containing 5 lakes. The lakes in TLW are in a chain. Batchawana Lake is the headwater lake at TLW (highest elevation, 497 m AMSL). It has two distinct basins, Batchawana Lake North and Batchawana Lake South. The water flows out of Batchawana Lake South to Wishart Lake (388 m AMSL) by Norberg Creek, then continues through Little Turkey Lake to Turkey Lake, and finally discharges into the Batchawana River (TLW website: http://www.tlws.ca/siteinfo/ lakes/ lakes.shtml). The watershed is completely underlain by sparingly soluble silicate bedrock (greenstones and granites) and is overlain by thin and discontinuous glacial till (Jeffries and Semkin, 1982; Semkin and Jeffries, 1983). The surface area (Ao) of the lakes have a range of 6 to 52 ha (Appendix 1), and the maximum depth (Zmax) have a range of 4.5 to 37.0 m. The mean surface area to mean maximum depth ratio (Ao/Zmax) is 1.33. DOC concentration in the five lakes ranged from 3.6 to 4.7 mg l^{-1}(1982-2002) (Appendix 1) and TLW received a high amount of SO_4 deposition each year (53.7 mEq m^{-2}. $year^{-1}$) (Table 2.2).

Figure 2.1. Location of the five study sites across Eastern Canada. Dorset, the Experimental Lakes Area (ELA), and Turkey Lakes Watershed (TLW) are located in Ontario. The Yarmouth and Kejimkujik sites are located in Nova Scotia (after analysis, Kejimkujik and Yarmouth were combined into one study site (NS)).

2.1.3. Experimental Lakes Area (ELA)

The ELA site is located within the Precambrian Shield in the northwestern region of Ontario. The region is remote, and removed from most anthropogenic disturbances. Most of the watersheds are uninhabited, with a few subjected to seasonal recreational use. These watersheds are typically characterized by thin, poorly-developed soils, and a dominant vegetation cover of black spruce and jack pine forests (Brunskill and Schindler, 1971). Four reference lakes (i.e., those that had not been manipulated) with long-term DOC data were available for analysis. The surface area (Ao) of the lakes have a range of 26 to 54 ha (Appendix 1), and the mean maximum depth (Zmax) have a range of 13 to 30 m. The mean surface area to maximum depth ratio (Ao/Zmax) is 1.68. DOC concentrations of the four lakes ranged from 3.0 to 6.7 mg l^{-1} (1982-2002) (Appendix 1) and The ELA site received the least amount of precipitation and SO_4 deposition (Table 2.2).

2.1.4. Kejimkujik and Yarmouth (NS)

The study lakes in southwestern Nova Scotia are located in the Kejimkujik and Yarmouth areas of Nova Scotia. Kejimkujik National Park is located on the Southern Upland of Nova Scotia, which is an area underlain by slates and granite. Much of the area is covered with fens and bogs. The forest consists of mixed coniferous and deciduous trees (Clair and Sayer, 1997; Parks Canada, 1998). Yarmouth is located on the Gulf of Maine in southwestern Nova Scotia. Both the Kejimkujik and Yarmouth areas are undeveloped, with 27 lakes in Kejimkujik and 11 lakes in the Yarmouth area. The surface area (Ao) of the lakes have a range of 3.8 to 685 ha in Kejimkujik and 14.8

to 100 ha in Yarmouth. The maximum depth (Zmax) have a range of 0.7 to 19.2 m in Kejimkujik and 1.5 to 12.4 m in Yarmouth, respectively (Appendix 1). The mean surface area to mean maximum depth ratio (Ao/Zmax) is 22.5 and 16.5, respectively. DOC concentrations ranged from 2.1 to 15.8 mg l^{-1} at Kejmkujik and from 2.7 to 16.2 mg l^{-1} at Yarmouth (1982-2002) (Appendix 1). Kejimkujik and Yarmouth received the greatest amount of precipitation and were the warmest sites with the shortest ice-cover period (Table 2.2) (1982-2002).

2.2. Parameters

The variables considered in this study are listed in Table 2.1. DOC and regional variables were provided by the Dorset Environmental Sciences Centre, the Freshwater Institute and Environment Canada. Global variables were obtained from the National Oceanic and Atmospheric Administration of the United States of America (http://www.cpc.ncep.noaa.gov/data/; http://www.arctic.noaa.gov/data.html).

2.2.1. Whole lake ice-free DOC concentrations

Whole lake ice-free DOC concentrations (mg l^{-1}, monthly mean), the dependent variable, were measured on 5 to 24 occasions per year from May to October at Dorset (1978-1998), ELA (1982-2002) and TLW (1982-2002). The concentration of DOC at Kejimkujik and Yarmouth consisted of one measurement at spring and one at fall overturn each year from 1982 to 2002. At Dorset, ELA and TLW whole lake DOC concentration was calculated by adding up the total mass of DOC in each layer and dividing by lake volume. The methods of measuring DOC concentrations are described by Hudson et al. (2003) for Dorset; by Stainton et al. (1977) for ELA; by Clair et al. (2008) for Kejimkujik and Yarmouth, and by APHA (2005, Technique 5310C and D) for TLW.

2.2.2. Regional variables

Regional independent variables included both climatic and non-climatic variables (Table 2.1): monthly total precipitation (PPTN, mm) which included snow and rainfall, daily mean air temperature (T, °C), sum of daily total solar radiation (TSR, KJ m^{-2}) which included ultraviolet radiation (UVR) and photosynthetically available radiation (PAR), and monthly total sulfate deposition from precipitation (mEq m^{-2}). All regional data was measured and calculated by research centres. However, ELA only provided hourly photosynthetically available radiation (PAR) from May to October. Therefore, hourly PAR data was converted to daily total PAR and then TSR was estimated by dividing PAR by 0.46 (Nagaraja Rao 1984) (The ratio of PAR over TSR was 0.53 at Dorset based on the data from 1982 to 1998). For the Kejimkujik and Yarmouth sites, TSR was obtained from a nearby station in Kentville, Nova Scotia.

2.2.3. Global variables

Three global variables were considered. The southern Oscillation Index (SOI), which described the monthly or seasonal fluctuations in the (atmospheric) pressure on the sea level between Tahiti and Darwin, Australia. The Pacific Decadal Oscillation (PDO) is a climate index used to describe the patterns of variation in sea surface temperature of the North Pacific (Mantua et al. 1997). It is often described as a longlived El Niño-like pattern of Pacific climate variability (Zhang et al. 1997). The North Atlantic Oscillation (NAO) is an index of winter climate variability in the North Atlantic region ranging from central North America to Europe. A positive NAO index phase is characteristic of warmer conditions in northern Europe and the northeast America. A negative NAO index phase is characteristic of colder air in northern Europe and the east coast of North American. Data for these three indices were obtained from The National Oceanic and Atmospheric Administration (NOAA) website http://www.cpc.noaa.gov/index.php; http://www.ldeo. columbia.edu/res/pi/NAO/).

Table 2.1. Variables considered in the study included five regional variables and three global indices. Each variable was divided into shorter time periods within a calendar year, such as one month, two months, and so on, until a full calendar year was completed. Each of these time periods was also lagged by one year for each independent variable.

Variable Considered	Unit
Dependent variable:	
Dissolved organic carbon (DOC)	Milligram (mg) l^{-1}
Independent variable:	
Daily mean total solar radiation (TSR)	KiloJoule (KJ) m^{-2}
Monthly total precipitation (PPTN)	Millimeter (mm)
Daily mean air temperature (T)	Celsius (°C)
Total sulfate deposition (SO_4)	milliEquivalents (mEq) m^{-2}
Pacific Decadal Oscillation (PDO)	Index
Southern Oscillation Index (SOI)	Index
North Atlantic Oscillation (NAO)	Index

Table 2.2. Mean ice-free dissolved organic carbon (DOC, mg l^{-1}) and regional variables: total solar radiation (TSR, KJ m^{-2}), precipitation (PPTN, mm), air temperature (T, °C) and SO_4 (mEq m^{-2}) for all sites during the study period. The coefficient of variation (CV) is listed for the mean DOC at each site. Kejimkujik and Yarmouth sites were later combined into the NS site. Measurements of SO_4 deposition were not available for the Yarmouth site, therefore, SO_4 from Kejimkujik was used for both sites once these sites were combined.

Variable	Dorset	TLW	ELA	Yarmouth	Kejimkujik	NS
Mean DOC (CV %)	3.4 (6.5)	4.2 (10.6)	5.0 (7.1)	5.7 (16.5)	7.3 (19.8)	6.6 (17.9)
TSR (May-Oct.) (CV %)	538 (5.0)	525 (4.1)	533 (7.5)	493 (6.4)	493 (6.4)	493 (6.4)
PPTN (May-Oct.) (CV %)	522 (17.0)	671 (15.8)	516 (21.8)	555 (20.6)	571 (17.3)	563 (18.2)
PPTN (annual total) (CV %)	1004 (10.4)	1224 (11.5)	704 (20.4)	1251 (11.7)	1332 (11.3)	1292 (10.6)
T (annual mean) (CV %)	4.7 (17.6)	4.5 (27.6)	2.9 (38.5)	7.1 (8.1)	6.8 (13.2)	6.9 (10.3)
SO_4 (annual total) (CV %)	55.9 (23.6)	53.7 (22.2)	16.9 (23.5)	---	29.6 (20.1)	29.6 (20.1)

CHAPTER 3: LONG-TERM PATTERNS OF DISSOLVED ORGANIC CARBON IN LAKES ACROSS EASTERN CANADA: EVIDENCE OF A PRONOUNCED CLIMATE EFFECT*

3.1. Introduction

Dissolved organic carbon (DOC) has multiple effects on the physical, chemical and biological processes that occur in lakes. One such fundamental role is that DOC, particularly colored DOC, selectively attenuates solar radiation (Bukaveckas and Robbins-Forbes 2000; Hargreaves, 2003; Maloney et al. 2005). This in turn affects the thermal environment and mixing depth of water bodies (Perez-Fuentetaja et al. 1999; Snucins and Gunn 2000). DOC strongly attenuates ultraviolet radiation (UVR) (Morris et al. 1995; Williamson et al. 1996) and has been shown to reduce harmful UVR damage to phytoplankton (Moeller 1994) and zooplankton (Molot et al. 2004; Rautio 2002). DOC also binds metals and nutrients, thereby influencing their bioavailability (Perdue 1998; Shaw et al. 2000). Furthermore, DOC is composed of many compounds that are used by microorganisms for energy (Anesio et al. 2005; Wetzel 2001). Therefore changes in DOC concentration can significantly affect multiple abiotic and biotic processes in lakes.

** Chapter 3 has been submitted for publication. Coauthors are: Jeff Hudson, Richard Neal, Thomas Clair, Michael Turner, Dean Jeffries, Peter Dillon, Lewis Molot, Keith Somers, and Ray Hesslein.*

There are in turn, many local and regional factors that affect the concentration and temporal patterns of DOC in lakes. DOC originates mainly from terrestrial systems and from in-lake processes (Aitkenhead-Peterson et al. 2003; Lennon 2004). The quality and quantity exported from terrestrial systems is affected by watershed properties, such as the proportion of wetlands (Dillon and Molot 1997; Hillman et al. 2004); vegetation type (Agren et al. 2007; Sobek et al. 2007), land use (Findlay et al. 2001; Mattsson et al. 2005), runoff (Dillon and Molot 2005) and geology, morphology and geography of the surrounding area (Hope et al. 1994; Moore 1998). Within-lake characteristics also affect DOC. For example, lake acidity and Fe concentration affect the rate of DOC photodecomposition (Anesio and Graneli 2003; Molot et al. 2005).

Despite growing concern over the effect of a changing climate on ecosystems, the long-term influences of regional and global variables on lake DOC are poorly understood. According to a handful of recent studies there is evidence that regional variables (e.g., precipitation, total solar radiation, sulfate deposition and temperature) affect long-term DOC patterns in water bodies. For example, models have been developed with climate-related variables (e.g., temperature and precipitation) and catchment variables to describe the dynamics DOC in surface waters (Correll et al. 2001; Futter et al. 2007). Evans et al. (2005) and Monteith et al. (2007) have reported an increase in DOC worldwide, with a corresponding decrease in sulfate deposition. However, these studies did not consider a full range of regional variables.

Hudson et al. (2003) included both regional and global scale variables to examine the long-term pattern in DOC in 8 lakes at Dorset (Ontario, Canada). Of the large number of regional and global variables considered, only photosynthetically available radiation (PAR) and precipitation were found to be strongly related to the long-term pattern in DOC in their lakes. Although short-term studies (e.g., days) had previously documented that solar radiation (both UV and visible) degraded DOC (Gennings et al. 2001; Molot et al. 2005), Hudson et al. (2003) was the first study to provide evidence that a negative long-term effect was present. However, the generality of the results of Hudson et al. to other sites beyond the Dorset lakes is not clear and further testing was warranted.

The present study tests the generality of the Hudson et al. (2003) results by examining the long-term pattern of DOC at additional sites across Eastern Canada. This analysis also included more regional and global variables.

3.2 Methods

3.2.1 Source of data and variables used

Whole-lake ice-free DOC concentration (mg l^{-1}) served as the dependent variable. The ice-free period consisted of DOC in lakes from May to October for all sites. Regional variables served as independent variables, which included regional climate, regional non-climate, and global-scale variables (Table 2.1). Each independent variable was analyzed in relation to whole lake ice-free DOC over various temporal periods: one month, two months, four months, six months and annually within the year of DOC measurement and also from the previous year (all period were lagged).

3.2.2. Synchrony of variables between lakes and sites

The long-term patterns of DOC in the study lakes within a site were analyzed for temporal coherence using Pearson correlation coefficients (Brien et al. 1984). If the temporal patterns were significantly synchronous for the study lakes within a site, then a mean DOC pattern was used to represent the temporal variation. Then we analyzed these mean patterns to determine if they were temporally coherent among study sites. This second analysis was to assess whether regional variables (e.g., climate variables) were also synchronous among study sites. This latter analysis was conducted to determine if sites could be combined into one site for the further analyses.

Monotonic trends in DOC and regional variables were identified with linear regression (Model I) for each site.

3.2.3. The relationship between DOC and regional variables

The relationships between the long-term pattern in DOC and the regional and global variables were examined using multiple linear regression analysis (MLR). Akaike's Information Criterion (AIC) was used to select the best model, as it is considered superior to traditional methods of model selection, particularly when many independent variables are being considered (Anderson et al. 2000). As our sample size (i.e., number of years in our time series) was relatively small in relation to the number of independent variables being considered, we calculated AICc, which is the second-order AIC that accounts for additional parameters, particularly when the ratio of sample size (n) to independent variables (k) is small (i.e., $n / k < \sim 40$) (Anderson et al. 2000; Burnham and Anderson 2002). We tested hundreds of models to evaluate the relationship between DOC and all possible combinations of independent variables over all designated time periods for each region. We then selected the top five models with the lowest AIC values for each site for further analysis (Burnham and Anderson 2002). The relative goodness of fit of these models for each site was determined by calculating their Akaike Weight (wi) and evidence ratio (ER) to determine if a single model was considerably better than the others for a region, or whether alternative models (competing models) were possible (Anderson et al. 2000). Only these 'best' models (the model with the lowest AIC value) and competing models (if present) are described in this paper. Statistical analyses were performed using Statistica (6.0), SPSS (13-15), SigmaPlot (9.0) and SAS (8.2). Data were tested for homogeneity of variance, normality, cross correlation for DOC, and auto-correlation between independent variables before any analyses were adopted.

3.3 Results

3.3.1. Regional characteristics

The eight Dorset lakes had the lowest average annual mean concentration of ice-free DOC (3.4 mg l^{-1}) and coefficient of variation (CV, 6.5 %) of all sites (Table 2.2 and Appendix 1). The average annual mean concentration of DOC in the 4 lakes at ELA and the 5 lakes at TLW were 5.0 mg l^{-1} (CV 7.1%) and 4.2 mg l^{-1} (CV 10.6%), respectively. Lakes at the Kejimkujik (27 lakes) and Yarmouth sites (11 lakes) had greater average annual mean DOC concentrations (7.3 and 5.7 mg l^{-1}, respectively), and greater variability in DOC (CV 19.8% and 16.5%, respectively) than the other sites (Table 3.1, and Fig. 3.1). Lakes at Kejimkujik and Yarmouth sites were the most acidic and those at ELA, the least acidic (Appendix 1).

During the study period, ELA received the least amount of precipitation annually. Conversely, Kejimkujik and Yarmouth received the most precipitation and the least amount of solar radiation (Table 2.2). SO_4 deposition was greatest at the Dorset and TLW sites (57.4 and 53.7 mEq m^{-2} $year^{-1}$, respectively). ELA was the coolest site with the greatest period of ice-cover, while NS (Kejimkujik and Yarmouth) was the warmest site with the shortest period of ice-cover (Table 2.2).

3.3.2. Synchronicity of patterns in DOC and regional variables

With one exception at Kejimkujik, the DOC patterns of all lakes at each site were temporally coherent ($P < 0.05$) (Table 3.1 and Fig. 3.2). Therefore, the lakes of each site (Fig. 3.2a) were merged into a single average DOC pattern (Fig. 3.2b). However, one lake (Upper Silver) at the Kejimkujik site was not temporally coherent with the mean DOC pattern of all 27 study lakes. This lake was excluded from further analysis.

The temporal patterns in DOC and regional variables (except for temperature) across sites were not temporally coherent, except for those between Kejimkujik and Yarmouth sites (Table 3.2). TSR data for Kejimkujik and Yarmouth sites were obtained from the same weather station, and therefore, temporal coherence in TSR between these two sites could not be analyzed. These two sites, located near each other, were combined into one and referred to as the NS site (Fig. 3.2). This resulted in the five study sites being reduced to 4 study sites: Dorset, ELA, TLW and NS. The average DOC patterns (i.e., one per region) were used in subsequent analyses.

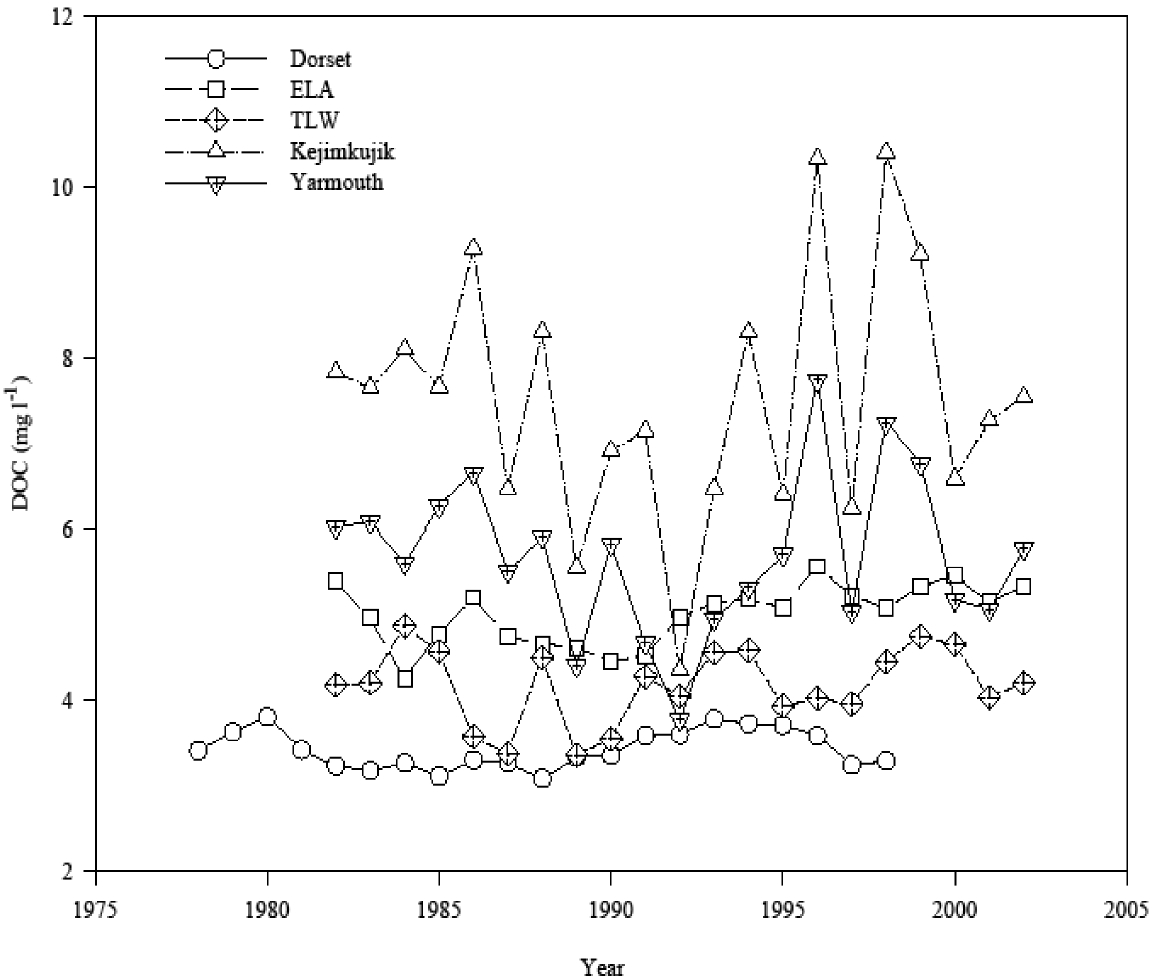


Figure 3.1. The mean ice-free DOC from May to October for all lakes at each site: Dorset, ELA, TLW and NS. Dorset had the lowest DOC concentration and interannual variation among sites, while NS had the highest DOC concentration and interannual variation.

3.3.3. Trends in DOC and regional variables

Interestingly, all sites appeared to have a cyclic DOC pattern (Fig. 3.2), where study periods started with higher DOC concentration, which then declined, and then increased, and then declined again near the end of the study period, except for ELA, where DOC concentration still appeared to be increasing at the end of the study period. Theses patterns were not completely synchronous across sites, i.e. the Dorset lake's pattern appeared more advanced in time (Fig. 3.2).

As a result, only ELA demonstrated an increase in its average ice-free DOC pattern (DOC = 0.03year + 4.7; P = 0.015) over the study period. Concomitantly at ELA, precipitation also increased (PPTN = 9.78year + 409; P = 0.012), while TSR decreased (TSR = -7.63year + 1046; P = 0.001) (Fig. 3.3). Temperature increased at TLW (P = 0.015) and NS (P = 0.04) sites (Fig. 3.3), but a concurrent trend in DOC, precipitation, and TSR was not evident at either site during the study period. SO_4 deposition declined at all sites ($P < 0.0003$) (Fig. 3.4). SO_4 declined more rapidly at Dorset (r^2=0.85, slope=-2.1, p<0.0001) and TLW (r^2=0.6, slope=-1.5, p<0.0001) (Fig. 3.4).

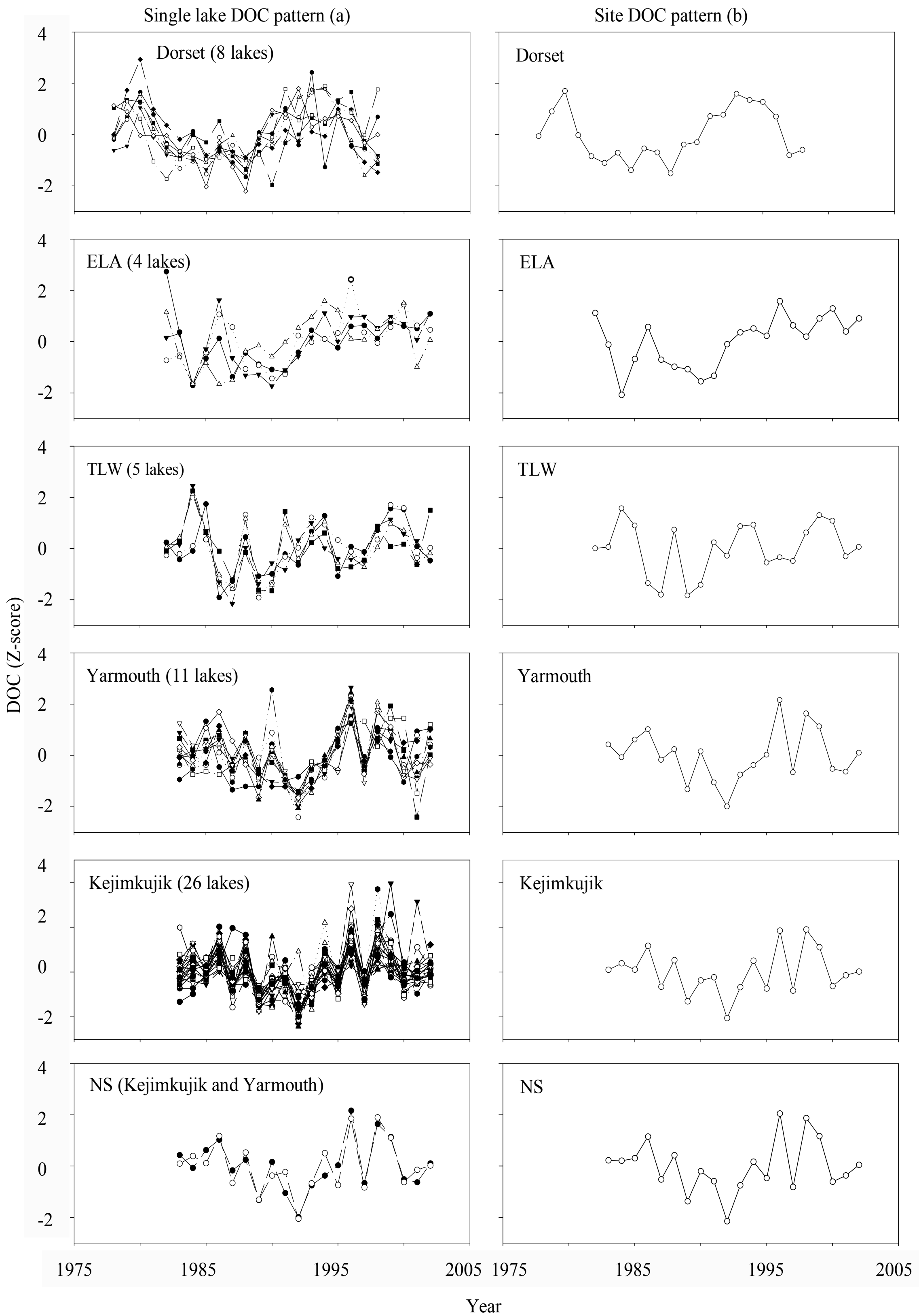
3.3.4. Single site models

The relationship between the average yearly ice-free DOC pattern (Fig. 3.3) and the independent variables (i.e., TSR, PPTN, T, SO_4, SOI, PDO and NAO) (Table 2.1) was analyzed with MLR and AIC. The best model(s) for each site is listed in Table 3.3.

Table 3.1. The temporal coherence among lakes at each site. The average and the range of the Pearson correlation coefficients for the temporal coherence analysis for each site are listed in columns 3 and 4. The variation in DOC for a single lake at a site was highly correlated to the average DOC pattern for that area. Upper Silver lake was excluded from the analysis because it was not temporal coherent with the other 26 lakes at Kejimkujik (* r = 0.37).

Area	Number of Lakes	Pearson correlation (r) Mean	Range
Dorset	8	0.78	0.60-0.96
ELA	4	0.77	0.55-0.89
TLW	5	0.85	0.75-0.94
Kejimkujik*	26	0.79	0.52-0.96
Yarmouth	11	0.77	0.49-0.92

Figure 3.2. Long-term ice-free DOC patterns in lakes at each site (a). Long-term patterns in DOC of all lakes within a site were temporally coherent (Pearson's correlation coefficient r, $P \leq 0.05$), except Upper Silver L. (Kejimkujik), which was removed from further analyses. The lakes at each site were combined and represented by a single average DOC pattern (b). DOC patterns between Kejimkujik and Yarmouth were temporally coherent ($r = 0.90$), therefore, these two sites were combined into one site (NS region). However, DOC patterns across the remaining sites were not temporally coherent, and were not combined.



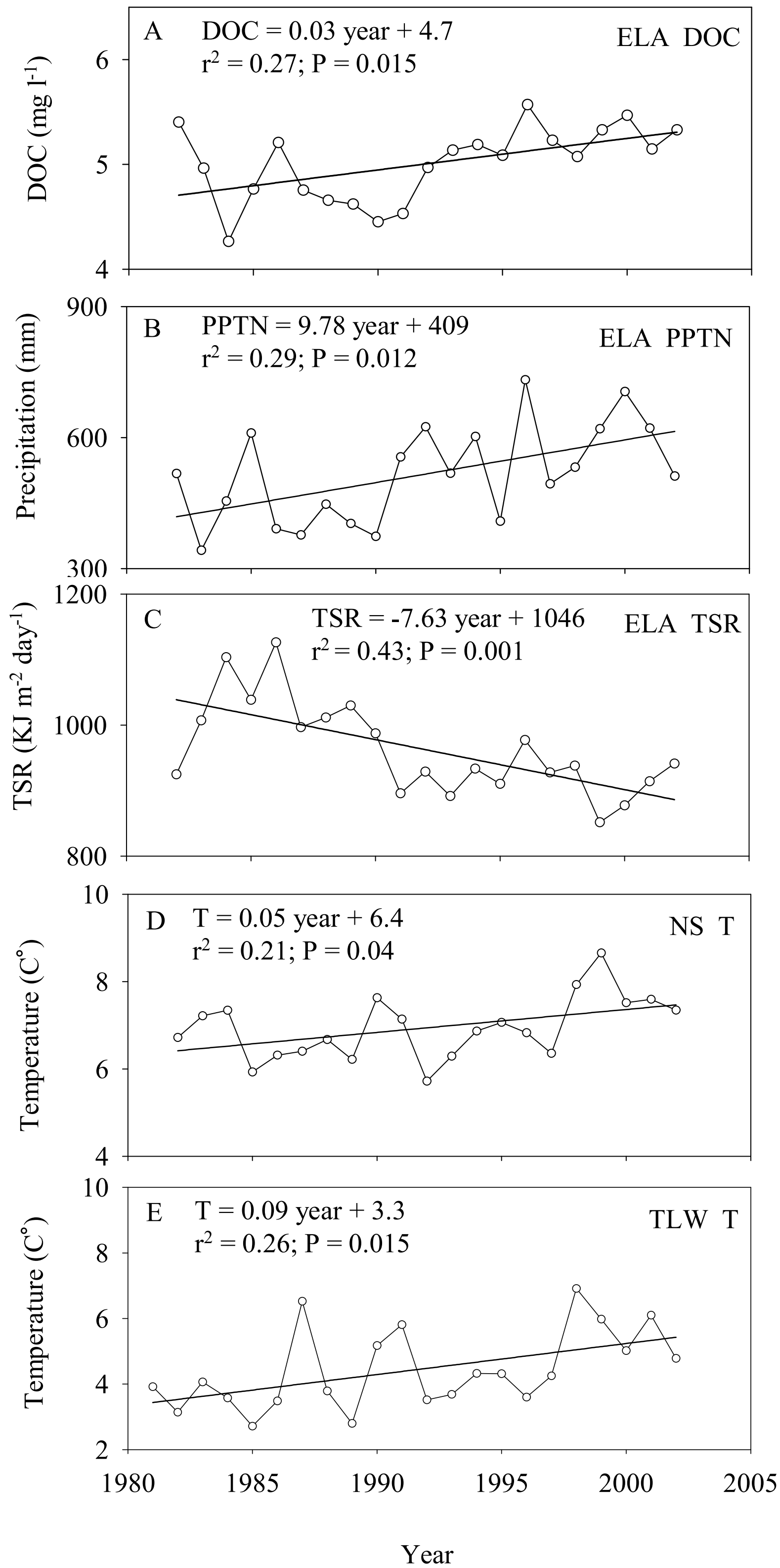
Single lake DOC pattern (a)
Site DOC pattern (b)
Dorset (8 lakes)
Dorset
ELA (4 lakes)
ELA
TLW (5 lakes)
TLW
Yarmouth (11 lakes)
Yarmouth
Kejimkujik (26 lakes)
Kejimkujik
NS (Kejimkujik and Yarmouth)
NS
DOC (Z-score)
Year
4
2
0
-2
1975
1985
1995
2005

Table 3.2. Results of temporal coherence analyses on the long-term pattern of variables between sites: DOC (ice-free), total solar radiation (TSR, May to October), precipitation (PPNT, annual) and temperature (T, annual). NS represents the combined site of Kejimkujik and Yarmouth. n.a., comparison not applicable.

		Pearson correlation coefficient (r)			
	Study area	Dorset	ELA	TLW	Yarmouth
DOC	ELA	0.23	1		
	TLW	-0.08	-0.02	1	
	Yarmouth	-0.13	0.33	0.11	1
	Kejimkujik	-0.23	0.27	0.32	0.90**
	NS	-0.21	0.30	0.26	n.a.
TSR	ELA	0.05	1		
	TLW	0.26	0.22	1	
	NS	0.21	-0.36*	-0.33	n.a.
Precipitation	ELA	0.22	1		
	TLW	0.35*	0.24	1	
	Yarmouth	0.16	0.04	-0.01	1
	Kejimkujik	0.27	0.03	0.28	0.74**
	NS	0.24	0.04	0.15	n.a.
Temperature	ELA	0.50**	1		
	TLW	0.42**	0.54**	1	
	Yarmouth	0.74**	0.55**	0.59**	1
	Kejimkujik	0.66**	0.55**	0.68**	0.91**
	NS	0.71**	0.56**	0.66**	n.a.

** Correlation is significant at the 0.01 level
* Correlation is significant at the 0.05 level.

Figure 3.3. Significant trends ($P<0.05$) of DOC and regional variables over the study period. At ELA the DOC concentration (A) and total precipitation (May to Oct.) have increased (B). However, total solar radiation (May to Oct.) at ELA has decreased (C). Annual mean air temperature has increased at NS and TLW sites (D and E).


A DOC = 0.03 year + 4.7
r2 = 0.27; P = 0.015
ELA DOC
DOC (mg l-1)
B PPTN = 9.78 year + 409
r2 = 0.29; P = 0.012
ELA PPTN
Precipitation (mm)
C TSR = -7.63 year + 1046
r2 = 0.43; P = 0.001
ELA TSR
TSR (KJ m-2 day-1)
D T = 0.05 year + 6.4
r2 = 0.21; P = 0.04
NS T
Temperature (C°)
E T = 0.09 year + 3.3
r2 = 0.26; P = 0.015
TLW T
Temperature (C°)
Year

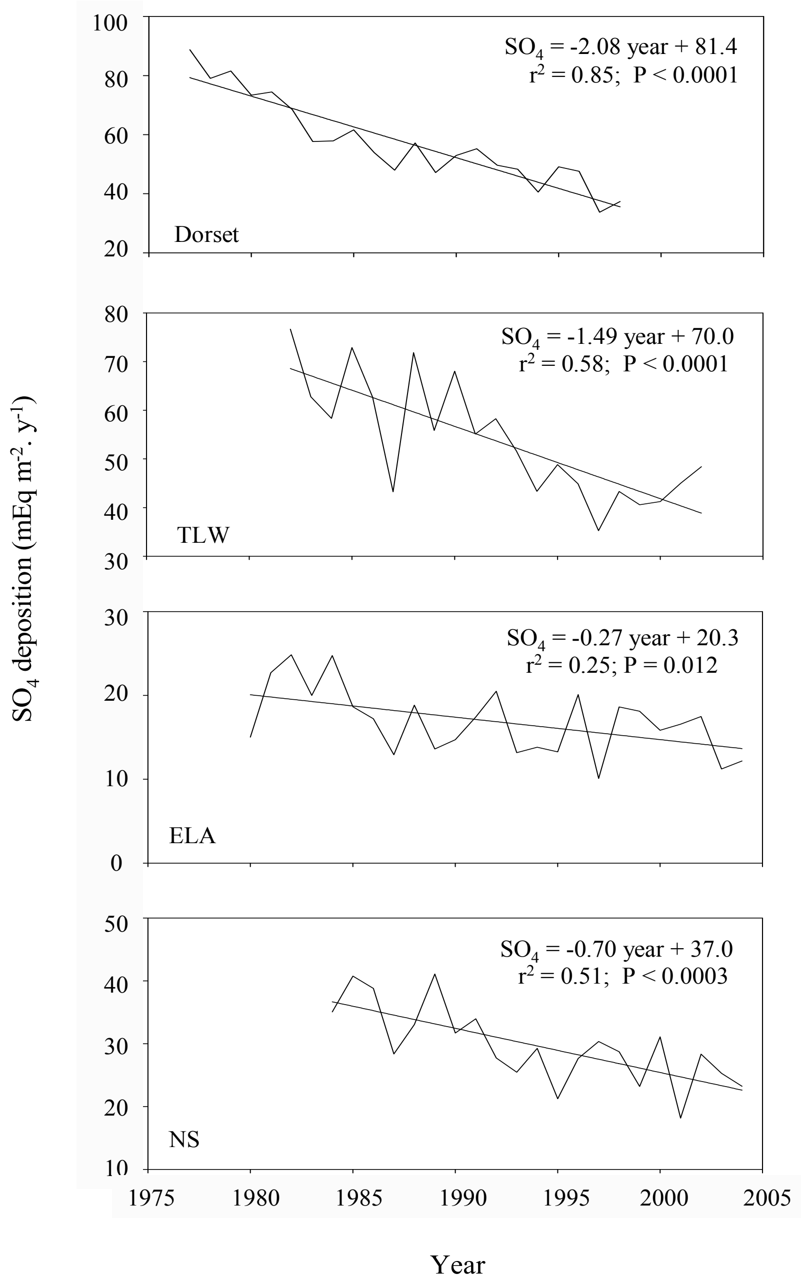


Figure 3.4. The trend in the long-term pattern in sulfate deposition (SO_4) at each site. Sulfate deposition decreased across all sites during the study period but the decline was much more rapid at Dorset and TLW.

Table 3.3. Independent variables (regional and global) that best describe the variation in the long term pattern in ice-free DOC at each region. Models were developed from multiple linear regression (MLR) analyses and Aikaikes Information Criterion (AIC). Only the best models (evidence ratio (ER) = 1) and competing models (2.7 > ER >1) are presented. The Aikaike weight (w_i) indicates which model is the best of the top five models for each site (total weight of five models = 1). Variation in the DOC pattern at the Dorset, ELA and NS sites was best described by only two regional variables: total solar radiation (TSR) and precipitation (PPTN). Little of the variation at the TLW site could be accounted for by regional climatic variables.

Site	Model	r^2	w_i	ER	Independent variable	Regression coefficient	Variance Explained (%)
Dorset	1	0.78	0.63	1	TSR (last Dec. - Feb.)	0.60	31
					PPTN (May. - Oct.)	0.51	26
					TSR (Jun. - Aug.)	-0.41	21
ELA	1	0.49	0.39	1	PPTN (Jul. - Aug.)	0.54	30
					TSR (May - Oct.)	-0.30	19
	2	0.41	0.28	1.43	PPTN (Jul. - Aug.)	0.64	41
NS	1	0.84	0.48	1	PPTN (May. - Oct.)	0.79	47
					TSR (annual mean)	-0.64	37
	2	0.85	0.25	1.96	PPTN (May. - Oct.)	0.75	46
					TSR (annual mean)	-0.57	32
					T (Feb. - May)	0.12	7
TLW	1	0.60	0.39	1	SOI (last Jan - Oct.)	-0.49	20
					PDO (Sep. - Oct)	-0.47	19

3.3.4.1. Dorset model

A single model was selected for Dorset (Table 3.3), which contained three variables that explained 78 % of the variation in the long-term pattern in DOC. DOC was negatively correlated with summer TSR (June to August), and positively correlated with both summer precipitation (PPTN, May to October) and winter TSR (last December to current February) (Table 3.3 and Fig. 3.5). Both temperature (T) and sulfate deposition (SO_4) were selected as minor variables in some of the top five models for this region, but not in the best model.

3.3.4.2. Experimental Lakes Area (ELA) model

Two possible models were selected for ELA (Table 3.3 and Fig. 3.6). The best model had two variables, summer precipitation (PPTN) from July to August (positive correlation with DOC) and total solar radiation (TSR) from May to October (inverse relationship with DOC) that together explained 49% of the variation in the long-term pattern of DOC. The alternative competing model only used precipitation (July to August), which explained 41% of the variation in DOC. Interestingly, precipitation during the ice-free period (May to October) was positively correlated to DOC at ELA as well, but the best model showed that DOC concentration was more sensitive to the changes in precipitation during the period of July to August. Temperature was also selected in some of the top models for this region, but not in the best model or the competing model.

Figure 3.5. Regional variables that best describe the variation in the long-term pattern of DOC at Dorset. (i) Mean summer daily total solar radiation (TSR, June to August) was negatively correlated with the long-term pattern in DOC. (ii) Mean winter daily total solar radiation (TSR, previous December to August) was positively correlated with the long term pattern in DOC. (iii) Total summer precipitation (PPTN, May to October) was positively correlated with the long-term pattern in DOC.

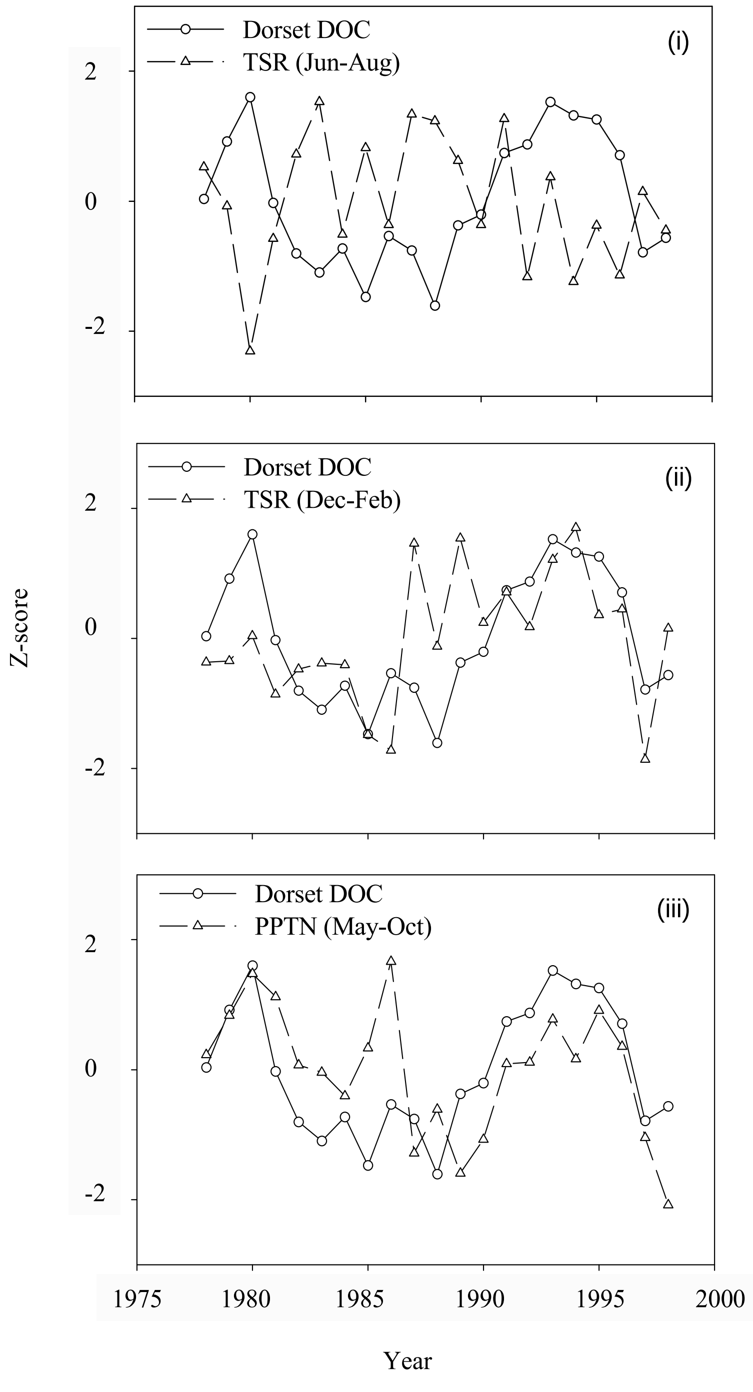

Dorset DOC
TSR (Jun-Aug)
(i)
Dorset DOC
TSR (Dec-Feb)
(ii)
Dorset DOC
PPTN (May-Oct)
(iii)
2
0
-2
Z-score
1975
1980
1985
1990
1995
2000
Year

Fig. 3a

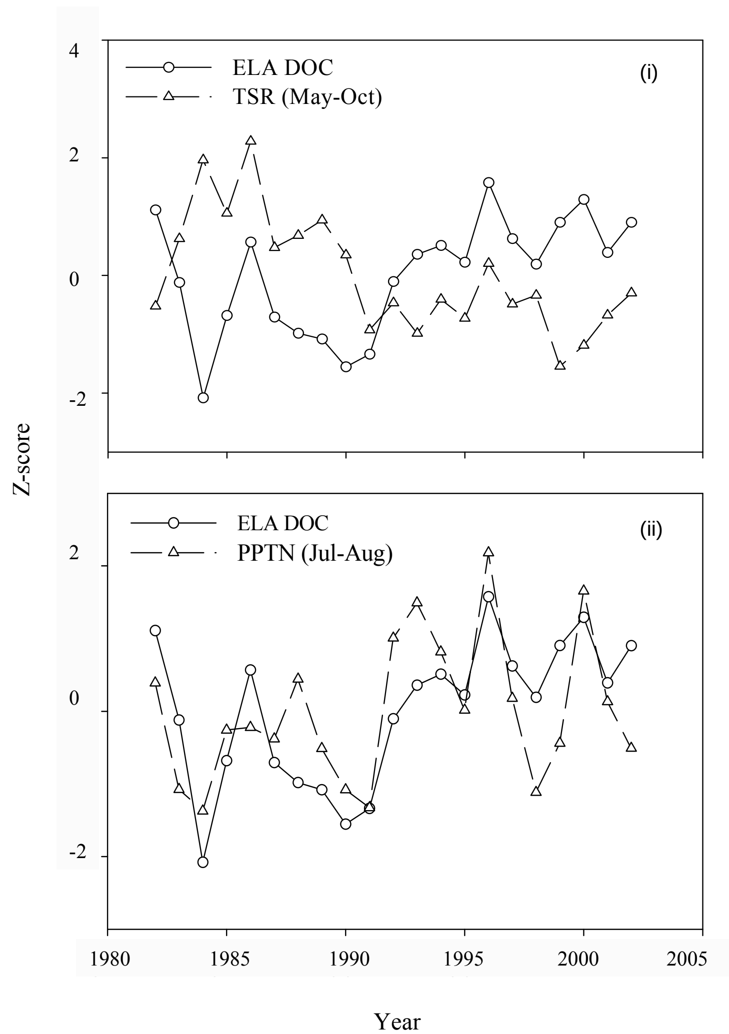


Figure 3.6. The two regional variables that best describe the variation in the long-term pattern of DOC at ELA. (i) Mean summer daily total solar radiation (TSR, May to Oct.) was negatively correlated with the DOC pattern, and (ii) total summer precipitation (PPTN, Jul. to Aug.) was positively correlated with the long-term pattern in DOC.

3.3.4.3. Nova Scotia (NS) model

Two possible models were selected for this site (Table 3.3 and Fig. 3.7). The best model contained two variables, TSR (annual mean) and precipitation (PPTN, May to October), which explained 84% of the variation in the long-term pattern in DOC. The alternative model added a third variable, the mean temperature (T) from February to May, which only increased the explained variation from 84% to 85% (Table 3.4). DOC was negatively correlated with TSR and positively correlated with summer precipitation (Table 3.3, Fig. 3.7). PDO and SOI were also selected in some of the top five models for this region, but not in the best model or the competing model.

3.3.4.4. Turkey Lake Watershed (TLW) model

Unlike the previous three sites, TSR and precipitation were not selected in the TLW model. Instead, the mean SOI (January to October of the previous year) and the mean PDO (September to October) were selected: these two independent variables explained 39% of the variation in the long-term pattern in DOC (20% by SOI and 19% by PDO). Both variables were negatively correlated with DOC at TLW (Table 3.3 and Fig. 3.8).

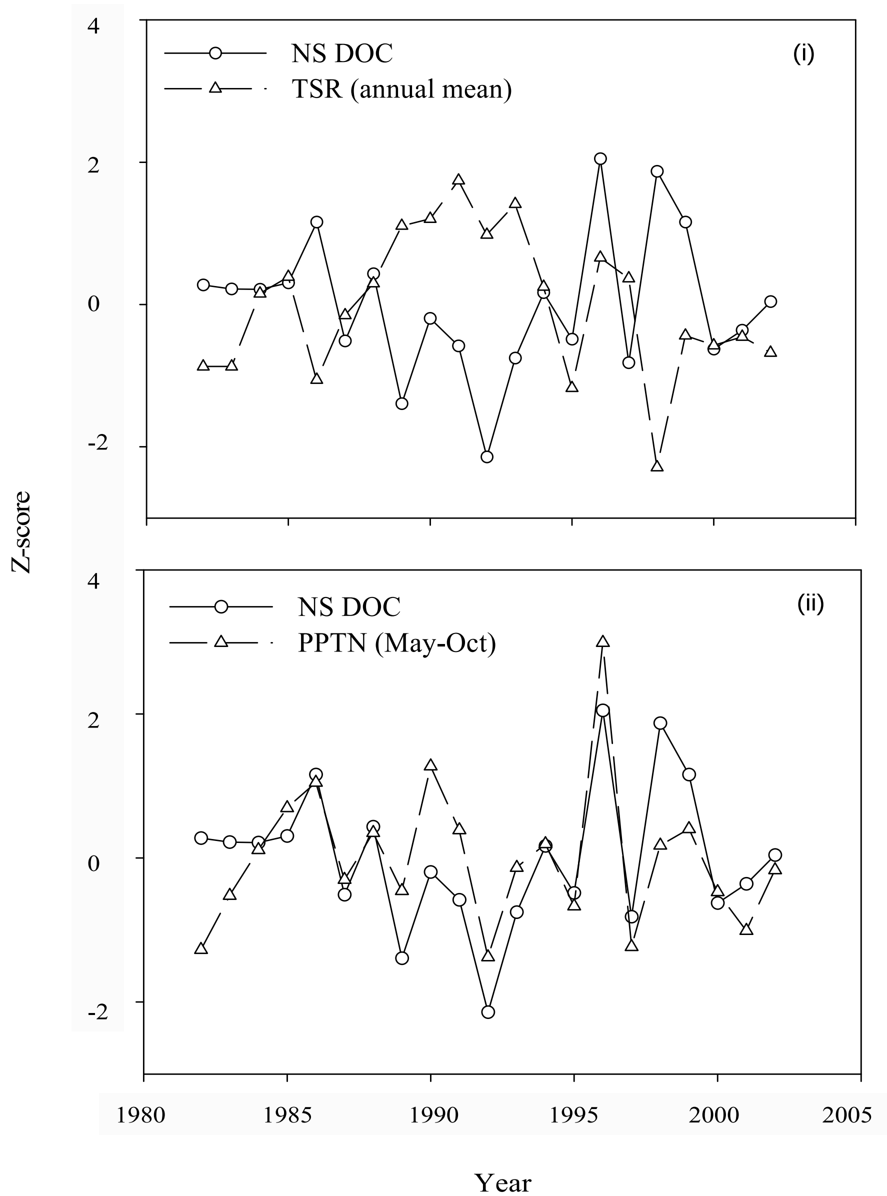


Figure 3.7. The two regional variables that best describe the variation in the long-term pattern of DOC at NS. (i) Annual mean daily total solar radiation (TSR) was negatively correlated with DOC pattern, and (ii) total summer precipitation (PPTN, May to October) was positively correlated with the long-term pattern in DOC.

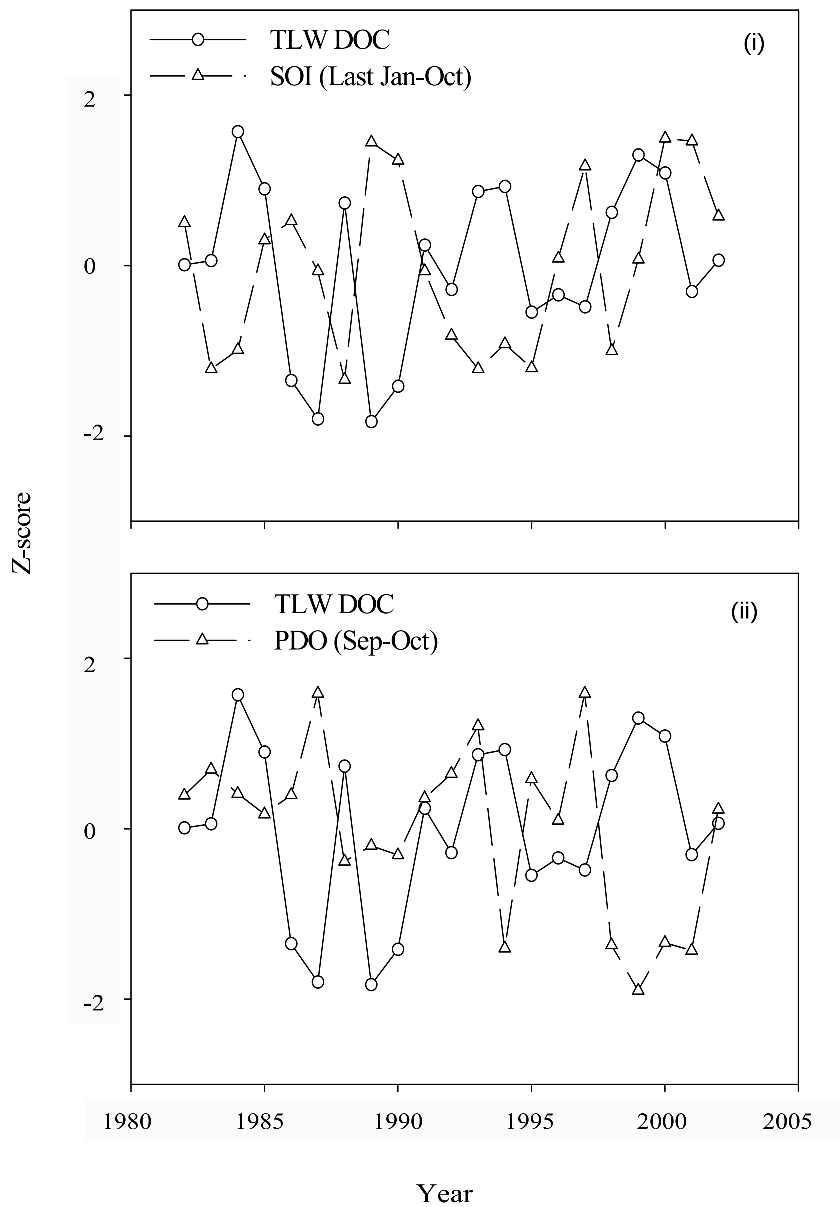


Figure 3.8. The two regional variables that best describe the variation in the long-term pattern of DOC at TLW. (i) Mean SOI (previous January to October) and (ii) PDO (September to October) were negatively correlated with the long-term pattern of DOC at TLW.

3.4 Discussion

3.4.1 Lake characteristics

Mean annual ice-free DOC concentration was greatest at the Nova Scotia site (Table 3.1 and Appendix 1). This may reflect the differences in climate and catchments between the Nova Scotia and the Ontario sites. For example, DOC concentration in lakes is directly related to the proportion of wetlands in a catchment (Dillon and Molot 1997) and the Nova Scotia study lakes do contain a greater proportion of wetlands in their catchments than the other study sites (Clair et al. 1994). In addition, the NS site receives more precipitation, which results in a greater export of DOC from catchment areas, and consequently, greater lake DOC concentrations, at least in lakes with low residence times (Clair et al. 2008).

3.4.2. Synchronicity of patterns in DOC and in independent variables

A synchronous DOC pattern was found among lakes within each of the 5 sites over the 21 year period (Fig. 3.2), indicating that an average DOC pattern could be used to represent the temporal variation of DOC for all lakes under study in each region. However, in the large scale inter-site comparison, only two of the five sites were synchronous in DOC: Kejimkujik and Yarmouth. Regional climate variables were also synchronous between Kejimkujik and Yarmouth (Table 3.3). Since the two sites are located only about 80 km apart, this might indicate that the temporal variation in DOC responded to a set of common variables within the overall area. In contrast, the temporal variations in DOC were not correlated between TLW, ELA, Dorset and NS, nor were their regional variables, except for temperature. This lack of correlation likely reflects the large distance between these sites, where regional climates (e.g. precipitation) vary considerably. This outcome further supports the understanding that regional variables, particularly precipitation (Magnuson et al. 1990; Pace et al. 2002) and TSR, are strong drivers of DOC patterns in northeast North American lakes (Hudson et al. 2003).

3.4.3. Trends in DOC

Additional years of data are required to determine if the cyclic pattern observed in Figure 3.2b for the four sites will continue beyond the years studied. For example, the most recent decline in DOC at three of the four sites may only represent short-term variability and not a long-term trend. However, if the cyclic pattern continues, then current explanations for the recent increases in DOC (e.g., decreases in sulfate deposition) in north east North America will have to be re-evaluated.

3.4.4. General relationships between DOC and regional variables

The models developed for the four sites (Table 3.3) suggest that the Turkey Lakes system was different from the other three sites, and so this site will be discussed separately. There were striking similarities in the models developed for Dorset, ELA, and NS. The concentration of DOC was positively correlated with summer precipitation and negatively correlated with summer TSR (or annual TSR in NS) across these three sites (Table 3.4). These correlations were independent of DOC concentration and variability (e.g., these factors were the lowest at Dorset and the greatest in Nova Scotia; Table 3.1 and Fig. 3.1), and were also independent of the values of solar radiation and precipitation (e.g., ELA had the least precipitation, and NS had the opposite conditions,

Table 3.1). The results were also consistent with the long-term trends observed at the ELA region, which was the only site where DOC showed a significant increase ($P = 0.015$) during the study period, with a concomitant increase in summer precipitation ($P = 0.0012$), and a decrease in summer TSR ($P = 0.001$, Fig. 3.3). Similar correlations were found in an earlier period (from 1972 to 1990) under opposite conditions (Schindler et al. 1996), that is, DOC declined when summer precipitation decreased, and summer solar radiation increased. This observation, together with the lack of long-term trends in DOC, precipitation and TSR at other sites, leads us to conclude that TSR and precipitation are the main factors responsible for changing DOC concentrations at these three sites. Summer precipitation likely increases DOC by exporting DOC into a lake from its surrounding watershed (Correll et al. 2001; Dillon and Molot 1997) and summer TSR likely decreases DOC by photochemical processes (Molot and Dillon 1997; Molot et al. 2005; Tzortziou 2007).

The negative correlation between DOC and TSR has been found in many short-term studies. Through photochemical processes, solar radiation, particularly UV, have been shown to cause reductions in DOC of approximately 20 – 60% over the course of days (11-70 days) (Andersen and Gjessing 2002; Shiller et al. 2006; Anesio et al. 2003; Molot et al. 2005). Hudson et al. (2003) compared the long-term DOC pattern with regional and global scale variables and determined that TSR had a negative correlation with the long-term DOC pattern in eight lakes in Dorset (central Ontario). Our results from multiple sites add further evidence to support and extend this negative relationship between TSR and DOC.

Precipitation was another important variable explaining changes in the long-term

DOC pattern and is a complex variable that influences DOC through indirect mechanisms. However, an increase in regional precipitation is expected to cause a greater loss of organic carbon from terrestrial systems (Clair et al. 1994) and a reduction in precipitation is thus expected to cause a decline in the export of DOC from terrestrial to aquatic systems (Schiff et al. 1998; Schindler et al. 1997) because DOC mass export and runoff are tightly coupled (Dillon and Molot (2005). This positive relationship between DOC and precipitation was found at ELA, Dorset and NS sites during summer. Summer precipitation can greatly increase stream and lake DOC concentrations (Easthouse et al. 1992; Hinton et al. 1997), particularly after a period of drought when the upper soil layers in a watershed become oxidized to produce labile DOC (Dillon and Molot 1997; Freeman et al. 2001).

Winter TSR was a strong positive predictor variable at Dorset (Table 3.4). The positive relationship between DOC and winter TSR at Dorset is not immediately intuitive. A strong inverse relationship ($P = 0.008$) between winter TSR and winter precipitation was previously found at the Dorset region (Hudson et al., 2003). Winters with greater precipitation and less TSR may result in the accumulation of more snow on the landscape which melts in the spring. The excess snow then increases spring flooding and thus increases DOC exports. Although spring flooding exports large loads of DOC, it also results in the dilution of DOC concentrations in the tributaries that are entering the Dorset lakes (see Figure 5 in Hudson et al. 2003) and thus dilutes lake DOC concentrations.

Temperature is synchronous across all sites, but DOC was not (Table 3.2 and Fig. 3.2). This demonstrates that the effect of temperature on the long-term pattern in DOC was weak compared to TSR and PPTN. Hongve et al. (2004) also found that variation in DOC was not correlated with temperature. However, other studies have found correlations between temperature and DOC. For example, rising temperatures associated with drought conditions resulted in reduced DOC loading to lakes (Dillon and Molot 1997; Schindler et al. 2005). In contrast, other studies have reported an increase in DOC export from greater decomposition rates occurring at higher temperatures (Freeman et al. 2001). However, these studies did not include solar radiation in their analyses, and temperature may become a less significant correlate when solar radiation is considered in these studies.

Besides precipitation, TSR and temperature, other regional and global variables were not significantly correlated or were only weakly correlated with the long-term DOC patterns. SO_4 deposition was not selected in any of the best or competing models in these three sites. Evans et al. (2005) have reported a significant increase in DOC during the recovery of European and some North American lakes from acidification, which is likely a consequence of a decline in acid-enhanced photo-oxidation rates occurring via the photo-Fenton pathway (Gennings et al 2001; Molot et al. 2005). Indeed, DOC increased rapidly in an experimentally neutralized acidified lake (Molot et al. 1990). This is consistent with our observations because TSR explained more of the variation in DOC in lakes of lower pH (e.g., in NS with a mean pH 5.5, TSR explained 38 % of variation in DOC; in ELA with a mean pH 7.0, TSR explained 19 %) (Appendix 1 and Table 3.4). However, we may not have captured the full effect of a decline in SO_4 deposition on DOC concentrations because SO_4 may take many years or decades to be exported to lakes where it would affect pH, and in turn, DOC photodecomposition rates (Dillon et al. 1996), particularly to these three sites where the watersheds are the main sources of lake DOC. Such delays in DOC response may not have been detected by our analyses which only considered time lags of one year or less.

Our results indicate that TSR and precipitation must be considered along with sulfate deposition when evaluating the acidification and recovery of lakes. As DOC is composed of natural organic acids, its concentration can significantly affect the acidity of boreal lakes which, in turn, affects DOC photo-mineralization rates (Molot et al. 2005). Many sites have reported increases in DOC (Driscoll et al. 2003; Evans et al. 2005). These increases in DOC may slow lake recovery from acidification. Although such increases in DOC have been attributed to reductions in sulfate deposition (Evans et al. 2006), our results suggest that changes in DOC may be related to a more complex set of regional variables. For example, are increases in DOC a result of a reduction in sulfate deposition, or a reduction in solar radiation, or an increase in precipitation, or a combination of all three in addition to other regional variables? As noted earlier, sulfate deposition has declined across all four of our sites, but only in the lakes from ELA, has DOC increased (Fig. 3.3) and this increase was more related to changes in TSR and precipitation than that of SO_4 deposition. However, as noted above, we may have found SO_4 deposition to be of greater importance if we had analyzed time lags exceeding one year. However, even this analysis may be inconsistent within and across sites because of the difference in retention of SO_4 in the watershed of each lake. The interplay between regional variables and lake acidity becomes even more complex when we consider climate warming which is expected to have major effects on the duration of ice cover in north-temperate lakes (Magnuson et al., 2000; Lofgren et al. 2002). Longer ice-free periods may expose lake DOC to greater amounts of solar radiation, and possibly result in greater photochemical losses of DOC.

3.4.5. Exception of TLW model

The model for TLW was different from those of the other three sites. It did not contain TSR and precipitation which were the common variables to the other three site-models. The five study lakes at TLW are all connected hydrologically in a series. Therefore, they are not fully independent of each other, and the temporal coherence found among these lakes may be a result of local factors instead of regional factors. Although SOI was included in the best model for the TLW region, this global-scale index was not strongly correlated with any of the long-term DOC patterns. The global indices describe world-wide weather patterns and may not always be good indicators of regional climate (Stenseth at el. 2003). For example, we found considerable differences in the climate patterns between sites (except temperature) in a relatively small area of the globe (Eastern Canada). As found elsewhere (Stenseth at el. 2003 and Hudson et al. 2003), long-term DOC patterns are better correlated to the climate of a site (i.e., precipitation) than global variables.

3.5. Conclusions

Long-term patterns in dissolved organic carbon concentrations in boreal lakes were characterized at five sites across eastern Canada. These patterns were further investigated to see if they may be explained by the long-term patterns in regional (e.g., climate) and global variables (e.g., SOI). The average ice-free DOC patterns in lakes at each study site were positively temporally coherent so that an average pattern could be used to represent the DOC dynamics of lakes within each region. However, DOC patterns across sites were not temporally coherent except between Kejimkujik and Yarmouth. Consequently, Kejimkujik and Yarmouth were combined to form one study region. Temperature was the only regional climatic variable that was synchronous across all sites, while average DOC, TSR, and precipitation were not synchronous. Therefore, the relationship between long-term DOC and the regional variables was modeled separately for the four regions. Subsequent analyses between DOC patterns and regional variables revealed that total solar radiation (TSR) and total precipitation (PPTN) explained the greatest amount of variation in DOC at three of the four study sites (range in r^2, 0.49 – 0.84). Summer TSR for Dorset and ELA, and annual TSR for NS were negatively related to the long-term DOC pattern. Summer precipitation also had a positive relationship with the long-term DOC pattern at all three sites. In addition, winter TSR had a positive relationship with the DOC pattern at Dorset. Outside of TSR and precipitation, the majority of regional and global variables were not closely related to the long-term mean annual ice-free DOC patterns. Our results provide further evidence that regional factors (e.g., solar radiation) significantly affect long-term DOC patterns in most of the boreal lakes. However, the long-term patterns in DOC in the lakes at TLW were not strongly correlated to regional variables. The reason for this exception of TLW may be caused by the unique characteristics of lakes at this study site.

We have highlighted the potential importance of regional factors on the long-term DOC patterns in lakes across eastern Canada. Future research may consider the factors that make some lake sites more sensitive to regional factors than others. For example, why was the variation in DOC at site NS better explained by regional factors than at ELA? We suspect that the long ice-free period and shallow lake morphometry (i.e., mean Ao/Zmax = 20) may render these NS lakes more sensitive to regional factors. We could not address this question quantitatively with our small sample size (i.e., four sites with only four climate regimes), but such an analysis would be possible with a larger number of sites (e.g., $n > 10$) that included a larger gradient in regional variables. In addition, such studies would be more complete if they also included local factors (i.e., catchment properties) in their analyses because local factors often modify a lake's response to regional factors. Finally, monitoring of lake water chemistry should be continued to identify any patterns (e.g., cycles) that may extend beyond the 21 year data set presented here. Additional years of sampling will also lessen the variability found in some parameters at certain sites (e.g. ice-free DOC at site NS).

CHAPTER 4. GENERAL REGRESSION MODEL FOR ALL SITES ACROSS EASTERN CANADA

4.1. Introduction

DOC varies not only temporally, but also spatially. Few studies have examined spatial variation in DOC. Dillon et al. (1997) and Xenopoules et al., (2003) found that the amount of wetland in a watershed was a significant predictor of spatial variation in DOC. Temnerud et al. (2007) and Brooks et al. (2007) evaluated the spatial variation in DOC along streams at many sites and found that landscape elements might cause variation in DOC between headwater and downstream locations. Sobek et al. (2007) examined over 7514 lakes, most of them located in North America and Europe. They analyzed the influence of topography and climate and found a negative relationship between altitude and lake DOC. They also found a negative relationship between lake DOC and runoff, which was the opposite relationship of that found in temporal studies (Hudson et al., 2003). This negative relationship may be based on spatial distribution, and not on temporal variation.

It should be noted that these studies are mainly concerned with the effects of local variables and the properties of watersheds on the spatial variation in DOC, rather than how the effects of climate or regional variables may affect DOC at different locations. The purpose of my study is to compare how multiple climatic and non-climatic (regional) variables relate to the long-term pattern in DOC at different sites across Eastern Canada.

In developing the individual site models in chapter 3 to explain the temporal variation in DOC, I noted that the models for Dorset, ELA and NS were similar, and the TLW site was different. We cannot use such an analysis to compare the strength of the response of DOC to regional variables across sites because the variances of the r^2 values of the response variables are not directly comparable. In order to directly compare the response of DOC to the main regional variables among sites I need to analyze all sites simultaneously as a single data set. With this approach, a general model may be developed to represent the spatial variation among these sites.

4.2. Methods

4.2.1. Variables and time periods selection

The dependent variable was whole lake DOC for the ice-free period from May to October, and the average value for all lakes at a site was used in the analysis (see chapter 3). The independent variables were daily total solar radiation (TSR, KJ m^{-2}), monthly total precipitation (PPTN, mm), daily mean air temperature (T, °C), monthly total sulfate deposition (SO_4, mEq m^{-2}), and three global variables: Southern Oscillation Index (SOI), North Atlantic Oscillation (NAO) and Pacific Decadal Oscillation (PDO).

4.2.2. Among site comparison of the response of DOC to regional variables

To compare the strength of the response of DOC to regional variables among sites, the data from all sites were combined and analyzed as one data set using a multiple linear regression approach. First, the qualified potential independent variables were selected to determine which linear correlations between DOC and regional variables were significant. Only the variables which had a significant linear correlation with DOC across sites were selected. If a site had no variables in common with other sites, it was excluded from the general model. A general model for a selected group of sites (i.e. those with common significant regional variables) was developed using multiple linear regression analysis (MLR) and Akaike's Information Criterion (AIC), in a the similar way to that described in chapter 3.

Two terms are used herein to describe the process of general model development: a complete model and a reduced model. A complete general model was developed in the following way. Each variable was entered multiple times individually for each site and the remaining sites given a categorical or dummy variable equal to 1. This complete data set is then analyzed using multiple linear regression (MLR). Then a series of reduced models are developed. For example, if there are three sites, (site code: a, b, and c), the variables were entered as pairs of sites (i.e. a+b, a+c, and b+c), and the remaining site is given a dummy variable of 1. Finally, the data are entered for all three sites (i.e. a+b+c) then simplified to combine all sites. Again, all these reduced data sets are analyzed using MLR. All models, including reduced and complete models are compared using AIC to determine the "best" general model.

4.3. Results

4.3.1. Independent variables and sites for the general model

Three sites, Dorset, ELA and NS, were selected to develop a general model. The TLW site was excluded in the general model, because TLW had no variables that were significantly correlated with DOC in common with any of the other three sites (Table

4.1). Two regional variables, TSR and precipitation, with certain time periods were selected as potential independent variables (Table 4.1). Other variables (temperature and sulfate deposition) were not significant across all three sites, and so were excluded from further consideration.

A preliminary comparison of DOC at the three sites showed that the average mean concentration of ice-free DOC and the year to year coefficient of variation (CV) of DOC was lowest at the Dorset site (mean DOC = 3.4 mg l^{-1}; CV =6.5%) and greatest at the NS site (mean DOC = 6.6 mg l^{-1}; CV = 17.9%), and the ELA site was intermediate (Table 3.1). Furthermore, the strength of the response of DOC to TSR and precipitation, as indicated by the slopes of the regression in Fig 4.1 and 4.2, were steeper at the NS site than the other two sites, which were similar to each other.

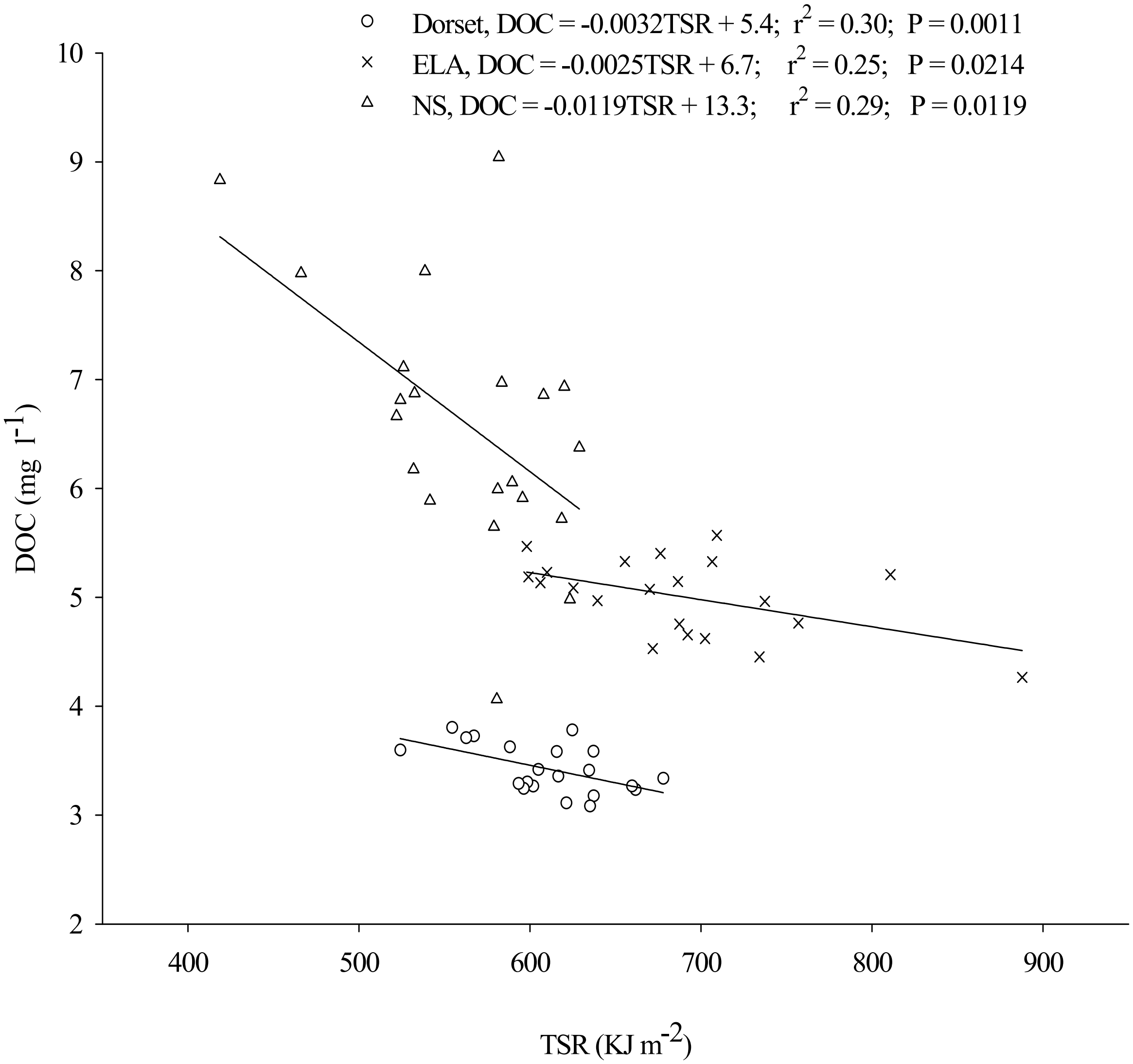


Figure 4.1. The response of DOC to TSR (daily average from July to August) for three sites: Dorset, ELA and NS (Nova Scotia). The responses were different between the three sites over a 21 year period (each site has its own intercept and slope).

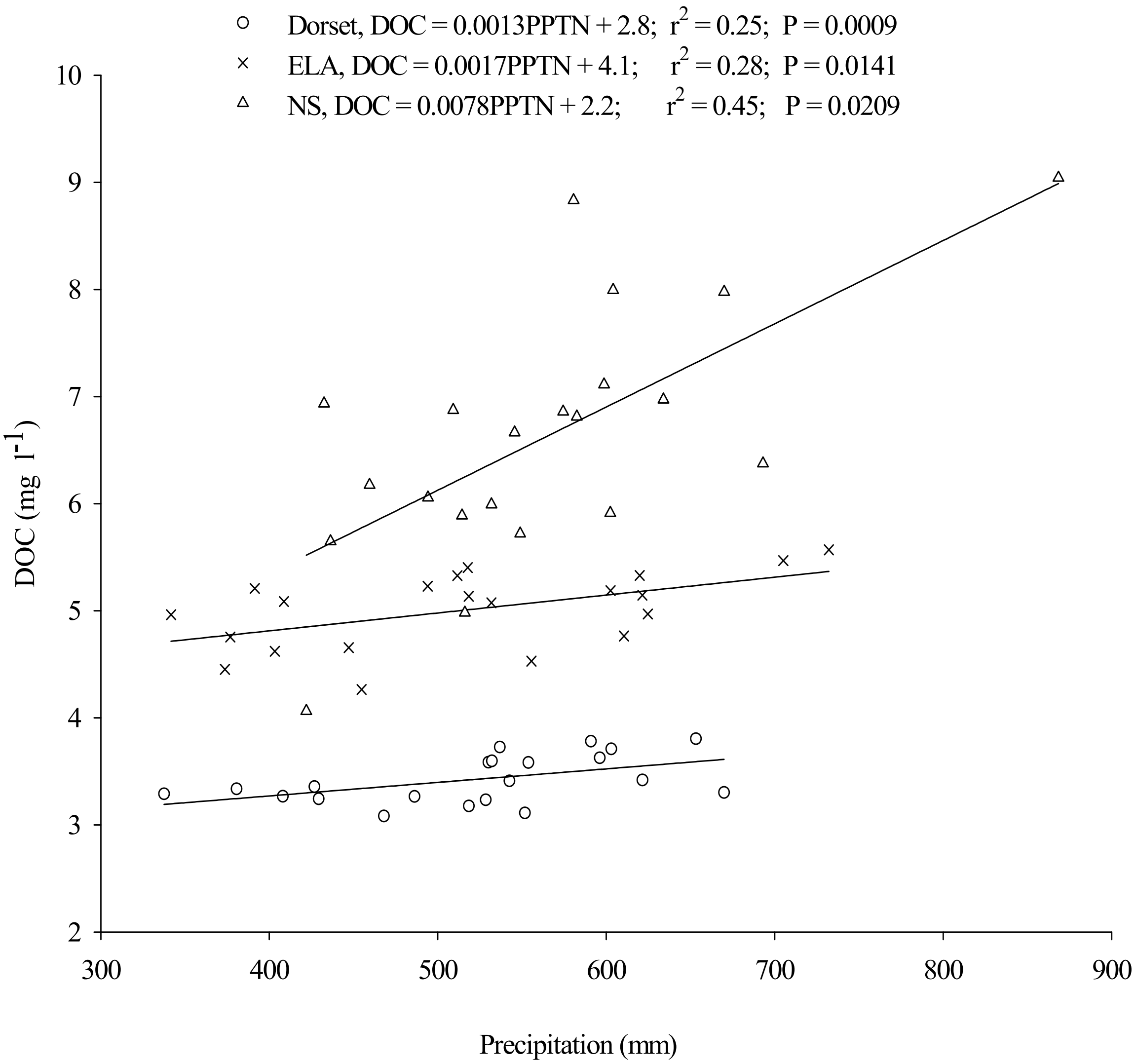


Figure 4.2. The response of DOC to precipitation (monthly total precipitation from May to October) for three sites: Dorset, ELA and NS (Nova Scotia). The responses were different between three sites over a 21 year period (each site has its own intercept and slope).

4.3.2. A general model for three sites

The best general models (with the lowest AIC value, see detail in Chapter 3) included TSR (July to August) and precipitation (May to October) as independent variables. The best complete general model indicated that the responses of DOC to TSR and precipitation for each site were included (Model 1, Table 4.2). A better reduced model was produced when the precipitation data for Dorset and ELA were combined (Model 2, Table 4.2), because the response of DOC to precipitation was similar at these two sites. However, because precipitation at these two sites explained so little variation (2%), the best general model was the reduced model 3 (Table 4.2), where precipitation at Dorset and ELA was excluded. Consequently, the best model was

$$DOC = -1.15\ TSR_{Dorset} - 0.63\ TSR_{ELA} - 1.54\ TSR_{NS} + 1.43\ PPTN_{NS}$$

$$r^2 = 0.91;\ P<0.0001$$

The temporal variation of DOC at the NS site explained 60% of the variation in the general model, and Dorset and ELA explained 31% of the variation. TSR at the three sites explained 56% of the variation in DOC in the general model, but the responses were significantly different among the three sites. Dorset contributed 20%, ELA 11%, and 26% to the general model respectively (Table 4.2). The responses of DOC to precipitation at ELA and Dorset were weak and could be ignored in the general model, but the response was very strong at NS and contributed about 34% of the explanation to the general model.

Table 4.1. The potential independent variables selected for the general model that have a significant linear relationship with DOC across all sites except for TLW. PPTN and TSR represent precipitation and total solar radiation, respectively.

		Dorset		ELA		NS		TLW	
Variable	Time period	Pearson r	*P*	Pearson r	*P*	Pearson r	*P*	Pearson r	*P*
PPTN	Ice-free	0.50	0.02	0.53	0.01	0.67	0.00	0.19	0.40
PPTN	Jun.-Aug.	0.51	0.02	0.50	0.02	0.44	0.04	0.06	0.81
PPTN	Jul.-Aug.	0.53	0.01	0.64	0.00	0.45	0.04	0.10	0.68
TSR	Jun.-Aug.	-0.60	0.00	-0.44	0.04	-0.49	0.02	0.04	0.86
TSR	Jul.-Aug.	-0.54	0.01	-0.50	0.02	-0.54	0.01	0.13	0.58

Table 4.2. General models developed for three sites. The complete model (Model 1) was progressively reduced to the best model (Model 3), which included TSR at all three sites and precipitation (PPTN) at NS only. * a, b and c are the codes for Dorset, ELA and NS, respectively.

Model	r^2	w_i	ER	Independent variable*	Coefficient	Variance explained (%)
1 (Complete)	0.92	0.06	10.1	$TSR_{Jul\text{-}Aug}$ a	-1.04	16
				$TSR_{Jul\text{-}Aug}$ b	-0.65	12
				$TSR_{Jul\text{-}Aug}$ c	-1.46	24
				$PPTN_{May\text{-}Oct}$ a	-0.02	0.4
				$PPTN_{May\text{-}Oct}$ b	0.12	3
				$PPTN_{May\text{-}Oct}$ c	1.44	36
2 (Reduced)	0.91	0.20	3.2	$TSR_{Jul\text{-}Aug}$ a	-1.13	20
				$TSR_{Jul\text{-}Aug}$ b	-0.62	11
				$TSR_{Jul\text{-}Aug}$ c	-1.48	23
				$PPTN_{May\text{-}Oct}$ ab	0.07	2
				$PPTN_{May\text{-}Oct}$ c	1.45	35
3 (Reduced)	0.91	0.69	1	$TSR_{Jul\text{-}Aug}$ a	-1.15	20
				$TSR_{Jul\text{-}Aug}$ b	-0.63	11
				$TSR_{Jul\text{-}Aug}$ c	-1.54	26
				$PPTN_{May\text{-}Oct}$ c	1.43	34

4.4. Discussion

4.4.1. Variables and sites for the general model

A general model could only be developed for three of the four sites (i.e. Dorset, ELA and NS), because the TLW site was different from the other sites. This is not surprising because a comparison of the specific site models in Chapter 3 showed that the model for the TLW site shared no independent variables with those of the other sites. The lakes at the TLW site were different from those of the other sites in that they had short water resident times and were located in a chain.

The general model for Dorset, ELA and NS only considered TSR and precipitation as independent variables because DOC had a significant linear correlation to these variables at all three sites for the time periods indicated in Table 4.1. Other variables or time periods were not included because either they were not significantly correlated across all sites (e.g. temperature and SO_4 deposition) or they were not available for all sites (e.g. winter TSR was not measured at the ELA site).

TSR (July to August) and precipitation (May to October) were selected as the key independent variables in the best general model. The time periods of these two variables are compared to those for the individual site models in Table 4.3. The general model has to compromise in selecting the time period when they differ among sites, and only the precipitation variables for Dorset and NS sites were the same in both the general and site models (Table 4.3). Consequently, the general model does not explain the variation in DOC of a particular site as well as the individual site models of chapter 3. The purpose of the general model is to compare the response of DOC to selected independent variables at different sites.

4.4.2. A general model for multiple sites

A general model can only be constructed if there is some level of similarity between sites. It was evident from the individual site models, developed in chapter 3, that there was some similarity between the models for Dorset, ELA and NS, but that TLW was completely different. So what information does the general model provide that is not already explained by the individual site models? If we consider the response of DOC to precipitation in the two types of models a very clear difference emerges. In the individual site models, precipitation explained 26% of the variation of DOC at Dorset, 30% of the variation at ELA, and 47% of the variation at NS (see Ch. 3). Obviously, precipitation was a strong independent variable at all three sites. However, in the general model, the effect of precipitation at Dorset and ELA was trivial (0.4% and 4%) and so was eliminated, whereas the effect remained strong for NS (34%). Why the difference? The general model compares the response of DOC to precipitation simultaneously at all three sites and so the r^2 values of general models are truly comparable between sites, which is not the case for the individual site models. The response of DOC to precipitation, as measured by the slopes of the regression in Fig. 4.3, clearly shows that precipitation has little affect on DOC at Dorset and ELA compared to NS. Thus, the general model gives a much better evaluation of the relative effects of the independent variables at different sites.

Table 4. 3. Key time periods of independent variables in the site-model and the general model.

Model	TSR	Precipitation
Site-model for Dorset	Jun - Aug and Last Dec -Feb	May - Oct
Site-model for ELA	May - Oct	Jul -Aug
Site-model for NS	Annual	May - Oct
General-model	Jul – Aug	May – Oct

The general model showed that the response of DOC to TSR was similar across the three sites (Table 4.2), but, as discussed above, the response of DOC to precipitation was overwhelmingly stronger at NS compared to the other two sites, the response of DOC to TSR was stronger at NS as well (Table 4.2). The NS site contributed 60 % of the explanation to the general model, while Dorset (r^2 of 20%) and ELA (r^2 of 11%) contributed much less to the explanation of the general model, because the responses of DOC to precipitation in both sites were weak.

The comparison of sites by the general model shows to what extent the sites are similar and how they differ, although this is only in terms of the variables that are included in the model. If one could compare numerous sites in this way it might better explain what site variables have an important influence on DOC. For example, there may be other sites that are similar to the TLW site, and an analysis of site parameters might prove fruitful to explain the lack of response to regional variables. In a similar fashion, one could develop a nested or hierarchical set of general models that might show the effects of size and nature of lake watersheds, the pH of the water, and other lake characteristics.

4.5. Conclusion

The best general model included TSR for all sites and precipitation at NS. The responses of DOC to precipitation at Dorset and ELA were similar, although the patterns of precipitation in both sites were different. These responses were weak and so both were excluded from the best general model. The responses of DOC to TSR and precipitation at NS dominated the general model. However, the responses of DOC to

TSR were strong and different across all three sites. Changes of TSR at each site would cause a change of DOC that would effect the variation among sites significantly.

CHAPTER 5. SUMMARY AND CONCLUSIONS

5.1. Summary of the patterns of variables

Overall, the DOC patterns of all lakes within sites were temporally coherent. Among the 55 lakes studied, there was only one exception in the Kejimkujik region. The DOC patterns in the rest of the 54 lakes could be grouped by sites and were merged into a single average DOC pattern for each site. Therefore, a single average DOC pattern was used to represent the temporal DOC pattern for each region. However, the average patterns among four of five sites were not temporally coherent. The one exception was between Kejimkujik and Yarmouth, which are only 80 km apart. The long-term patterns in DOC and the climatic and non-climatic variables were both temporally coherent at Kejimkujik and Yarmouth. Consequently, these two sites were combined into one study site, and this reduced the five sites to four study sites.

Of the regional variables, only temperature, showed synchronous changes over time at all four study sites. In addition, SO_4 deposition declined at the four sites, declining most rapidly during the study period at Dorset and TLW. However, no detectable long-term trends were found in the ice-free DOC measurements except at ELA, where DOC increased over the study period. However, during this period at ELA, precipitation also increased while TSR decreased (Schindler at al., 1996). Daily mean temperature significantly increased at the TLW and NS sites, but there was no associated trend in DOC. I concluded that this evidence supports that changes in the long-term DOC patterns in my study lakes are primarily related to changes in TSR and precipitation, not by decreases in SO_4 deposition or changes in temperature.

5.2. Summary of the individual site-models

TSR and precipitation were found to be the most important variables explaining the variation of the long-term pattern of DOC at three of the four sites across eastern Canada. Summer TSR was found to have a negative relationship with DOC, while precipitation had a positive relationship with DOC. TSR and precipitation explained 78%, 49% and 84% of the variation of the long-term DOC patterns at Dorset, ELA and NS, respectively. The contribution of summer TSR (annual TSR for NS) to their models was high at NS (37%) and low at ELA (19%), which was associated with the gradient in pH values across these three sites. The lakes at NS were more acidic (pH of 5.3), while the lakes at ELA were less acidic (pH of 7.0). This supports the results found by Molot et al (2005) that acidic water accelerates the loss of DOC through photochemical processes. An increase in summer precipitation resulted in an increase in lake DOC in these three sites.

Because of the unique characteristics of the lakes at TLW, the model for TLW was different from other sites. It did not include any regional variables, instead, it included two global variables, the mean SOI (January to October of the previous year) and the mean PDO (from September to October). These two variables explained 39% of the temporal variation of DOC. SOI explained 20% and PDO another 19% of the variation in DOC at TLW. Both variables were negatively correlated with DOC.

SO_4 deposition was not found to have a strong correlation with the temporal DOC pattern of this study, and was not selected by any best site-models. However, some studies have reported that a decrease in SO_4 should cause an increase in DOC because the water would become less acidic. However, SO_4 may take many years to be exported to lakes where it would affect pH, and in turn DOC photodecomposition processes. Consequently, such delays in DOC response may not have been detected by my analysis because it only considered time lags of one year or less. The variables with a synchronous pattern across all sites, such as temperature, SOI, PDO and NAO were not found to explain the variation in DOC over time.

5.3. Summary of the general model

The general model explored the strength of the response of DOC to the regional variables across sites. This could only be done for variables that were significantly correlated across all sites. The TLW site was excluded from the general model because none of the regional variables were correlated with those of the other sites. Consequently, a general model was developed from a combined data set for three sites: Dorset, ELA and NS. It evaluated the variables which influenced the site-to-site variation of DOC among three sites and compared the similarity of the responses to determine which one contributed the most to the (site-to-site) variation of the DOC across sites. The best general model suggested that 91% of the (site-to-site) variation of DOC among sites could be predicted by summer TSR of all sites and precipitation at NS. TSR from three sites explained 57%, and precipitation at NS explained 34% of the site-to-site variation of DOC. Precipitation from Dorset and ELA had a very weak effect on the variation and were excluded from the best general model. The stronger responses of DOC to the environmental changes at NS resulted in NS dominating the general model (r^2 of 60%), whereas Dorset (r^2 of 20%) and ELA (r^2 of 11%) contributed much less to the explanation of the general model.

5.4. Further Discussion

Unlike past studies, my study considered multiple regional variables at multiple sites for a period of 21 years. Analyzing the effects of multiple variables on DOC at one site allowed the comparison of the strength of the responses of DOC to those regional variables, and was better able to determine the key predictor variables than those studies which considered only a limited number of variables and often for shorter periods of time. In addition, the study of multiple sites in the same way allowed me to check the consistency of the models, which resulted in stronger conclusions than could be made by studying just a single site. For example, at the ELA site the long-term (21 year) changes in DOC appeared to be associated with a decrease in SO_4. However, this association was not seen at other sites, and the analysis showed that the changes in DOC at ELA were better explained by changes in TSR and precipitation.

This study has highlighted the potential importance of regional factors on the long-term DOC patterns in lakes across eastern Canada. Future research may consider the factors that make some lake sites more sensitive to regional factors than others. For example, why was the variation in DOC at NS better explained by regional factors than at ELA? I suspect that the long ice-free period and shallow lake morphometry (i.e., mean Ao/Zmax = 20) may render these NS lakes more sensitive to regional factors. I could not address this question quantitatively with this small sample size (i.e., four sites with only four climatic regimes), but such an analysis would be possible with a larger number of sites (e.g., $n > 10$) that included a larger gradient in regional variables. In addition, such studies would be more complete if they also included local factors (i.e., catchment properties) in their analyses because local factors often modify a lakes response to regional factors. Finally, monitoring of lake water chemistry should be continued to identify any patterns (e.g., cycles) that may extend beyond the 21 year data set presented here and to reduce variability in the current data set.

REFERENCES

Aarnos, H., P. Ylöstalo and A. Vähätalo. 2007. Photodegradation of dissolved organic matter (DOM) in the Baltic Sea. Geophysical Research Abstracts 9, 02689.

Agren, A., I. Buffam, M. Jansson, and H. Laudon. 2007. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. Journal of Geophysical Research-Biogeosciences 112 (G3): Art. No. G03003.

Aitkenhead-Peterson, J.A., W.H. McDowell, and J.C. Neff. 2003. Sources, Production, and Regulation of Allochthonous Dissolved Organic Matter Inputs to Surface Waters, p. 25 - 70, *In* C. S. Findlay and R. L. Sinsabaugh, eds. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Academic Press, San Diego, California.

Amon, R.M.W., and R. Benner. 1996. Bacterial utilization of different size classes of dissolved organic matter. Limnol. Oceanogr. 41: 41-51.

Andersen, D.O., and E.T. Gjessing. 2002. Natural organic matter (NOM) in a limed lake and its tributaries. Water Res. 36: 2372-2382.

Anderson, D.R., K.P. Burnham, and W.L. Thompson. 2000. Null hypothesis testing: problems, prevalence, and an alternative. J Wildlife Manage 64: 912-923.

Anesio, A.M., and W. Graneli. 2003. Increased photoreactivity of DOC by acidification: Implications for the carbon cycle in humic lakes. Limnol. Oceanogr. 48: 735-744.

Anesio, A.M., W. Grane´li, G.R. Aiken, D.J. Kieber, and K. Mopper. 2005. Effect of humic substance photodegradation on bacterial growth and respiration in lake water. Appl Environ Microb. 71 (10): 6267-6275.

Bancroft, B.A., Baker, Nick J., Blaustein, Andrew R., 2007. Effects of UVB radiation on marine and freshwater organisms: a synthesis through meta-analysis. Ecology Letters 10: 332-345.

Bertilsson, S., and J.B. Jones Jr. 2003. Supply of Dissolved Organic Matter to Aquatic Ecosystems: Autochthonous Sources, p. 3 - 24, *In* S. E. G. Findlay and R. L. Sinsabaugh, eds. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Academic Press, San Diego, CA.

Bilby, R.E. 1981. Role of Organic Debris Dams in Regulating the Export of Dissolved and Particulate Matter from a Forested Watershed. Ecology 62 (5): 1234-1243.

Bringolf, R.B., B.A. Morris, C.J. Boese, R.C. Santore, H.E.A. HE, and J.S. Meyer. 2006. Influence of dissolved organic matter on acute toxicity of zinc to larval fathead minnows (Pimephales promelas). Arch Environ Con Tox 51: 438-444.

Brooks, M.L., Meyer, Joseph S., McKnight, Diane M.. 2007. Photooxidation of wetland and riverine dissolved organic matter: altered copper complexation and organic composition. Hydrobiologia 579: 95-113.

Brunskill, G.J., and D.W. Schindler. 1971. Geography and Bathymetry of Selected Lake Basins, Experimental Lakes Area, Northwestern Ontario. J Fish Res Board Can 28 (2): 139-155

Bukaveckas, P.A., and M. Robbins-Forbes. 2000. Role of dissolved organic carbon in the attenuation of photosynthetically active and ultraviolet radiation in Adirondack lakes. Freshwater Biol 43: 339-354.

Burnham, K.P., and D.R. Anderson. 2002. Model selection and inference: a practical information-theoretic approach, 2nd edition Springer-Verlag New York Inc., New York.

Burton T.M. and Allan J.W.1986. Inflence of pH, aluminum, and organic matter on stream invertebrates. Can J Fisheries and Aquat Sci. 43: 1285-1289

Carignan, R., P. D'Arcy, and S. B. Lamontagne. 2000. Camparative impacts of forest fire and forest harvesting on water quality in Boreal Shield Lakes. Can. J. Fish. Aquat. Sci (suppl.2) 57: lO5-1 17.

Carpenter, S., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith. 1998. Nonpoint Pollution of surface Waters with Phosphorus and Nitrogen. Issues in Ecology 3, summer:1-12.

Christensen, D.L., B.R. Herwig, D.E. Schindler, and S.R. Carpenter. 1996. Impacts of lakeshore residential development on coarse woody debris in North Temperate Lakes. Ecol Appl 6:1143-1149.

Clair, T.A., and J.M. Ehrman. 1996. Variations in discharge and dissolved organic carbon and nitrogen export from terrestrial basins with changes in climate: A neural network approach. Limnol. Oceanogr. 41: 921-927.

Clair, T.A., and B.G. Sayer. 1997. Environmental variability in the reactivity of freshwater dissolved organic carbon to UV-B. Biogeochemistry 36: 89-97.

Clair, T.A., T.L. Pollock, and J.M. Ehrman. 1994. Exports of carbon and nitrogen from river basins in Canada's Atlantic Provinces. Global Biogeochem Cy 8: 441-450.

Clair, T.A., I.F. Dennis, P.G. Amiro, and B.J. Cosby. 2004. Past and future chemistry changes in acidified Nova Scotian Atlantic salmon (Salmo salar) rivers: a dynamic modeling approach. Can J Fisheries and Aquat Sci 61: 1965-1975.

Clair, T.A., I.F. Dennis, R. Vet, and H. Laudon. 2008. Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada. Biogeochemistry 87: 83-97.

Cole, J.J., G.E. Likens, and D.L. Strayer. 1982. Photosynthetically Produced Dissolved Organic Carbon: An Important Carbon Source for Planktonic. Bacteria 27(6): 1080-1090.

Cooper, W., and D. Lean. 1989. Hydrogen peroxide concentration in a northern lake: photochemical formation and diel variability. Environ Sci Technol 23: 1425-1428.

Correll, D., J.T. E., and D.E. Weller. 2001. Effects of precipitation, air temperature, and land use on organic carbon discharges from Rhode River watershed. Water Air Soil Poll 128: 139-159.

Curtis, P.J. 1998. Climatic and Hydrologic control of DOM concentration and quality in lakes, p. Chapter 4, pp 93-105, *In* T. Hessen, ed. Ecological Studies, Vol. 133. Springer-Verlag, Berlin, Heidelberg.

Dillon, P.J., and L.A. Molot. 1990. The role of Ammonium and Nitrate Retention in the Acidification of lakes and Forested Catchments. Biogeochemistry 11: 23-43.

Dillon, P.J., and L.A. Molot. 1997. Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. Water Resour Res 33(11): 2591-2600.

Dillon, P.J., L.A. Molot, and M. Futter. 1997. The effect of El Nino-related drought on recovery of acidified lakes. Environ Monit Assess 46: 105-111.

Dillon, P.J., and H.E. Evans. 2001. Comparison of iron accumulation in lakes using sediment core and mass balance calculations. Sci Total Environ 266: 211-219.

Dillon, P.J., K.M. Somers, J. Findeis, and M.C. Eimers. 2003. Coherent response of lakes in Ontario, Canada to reductions in sulphur deposition: the effects of climate on sulphate concentrations. Hydrol Earth Syst Sc 7(4): 583-595.

Dillon, P.J., and L.A. Molot. 2005. Long-term trends in catchment export and lake retention of dissolved organic carbon, dissolved organic nitrogen, total iron and total phosphorus: The Dorset, Ontario study, 1978-1998. J Geophys Res – Biogeosciences 110, No.G01002, doi:1029/2004JG000003.

Driscoll, C.T., D. Whitall, J. Aber, E. Boyer, M. Castro, C. Cronan, C.L. Goodale, P. Groffman, C. Hopkinson, K. Lambert, G. Lawrence, and S. Ollinger. 2003. Nitrogen pollution in the northeastern United States: Sources, effects, and management options. Bioscience 53: 357-374.

Easthouse, K.B., J. Mulder, N. Christophersen, and H.M. Seip. 1992. Dissolved organic carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, Southern Norway. Water Resour Res 28(6): 1585-1596.

Eckhardt, B.W., and T.R. Moore. 1990. Controls on dissolved organic carbon concentrations in streams, southern Qu,bec. Can J Fisheries and Aquat Sci 47: 1537-1544.

Elder, J.F., Nancy B. Rybicki, Virginia Carter, and Victoria Weintraub 2000. Sources And Yields Of Dissolved Carbon In Northern Wisconsin Stream Catchments With Differing Amounts Of Peatland. Wetlands 20: 113-125.

Engstrom, D. 1987. Influence of Vegetation and Hydrology on the Humus Budgets of Labrador Lakes. Can J Fisheries and Aquat Sci. 44: 1306-1314.

Evans, C.D., D.T. Monteith, and D.M. Cooper. 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. Environ Pollut. 137: 55-71.

Evans, C.D., P.J. Chapman, J.M. Clark, D.T. Monteith, and M.S. Cresser. 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. Global Change Biology 12: 2044-2053.

France, R., R. Steedman, R. Lehmann, and r. Peters. 2000. Landscape modification of DOC concentration m boreal lakes: Implications for UV-B sensitivity. Water Air Soil Poll. 122: 153-162.

Findlay, S., J.M. Quinn, C.W. Hickey, G. Burrell, and M. Downes. 2001. Effects of land use and riparian flowpath on delivery of dissolved organic carbon to streams. Limnol. Oceanogr. 46(2): 345-355.

Francko, D.A. 1986. Epilimnetic phosphorus cycling: influence of humic materials and iron on coexisting major mechanisms. Can J Fisheries and Aquat Sci. 43: 302-310.

Freeman, C., C.D. Evens, D.T. Monteith, B.Reynolds, and N. Fenner. 2001. Export of oganic carbon from peat soils. Nature 412: 785.

Frost, P.C., J. H. Larson, C. A. Johnston, K. C. Young, P. A. Maurice, G. A. Lamberti, and S. D. Bridgham. 2006. Landscape predictors of stream dissolved organic matter concentration and physicochemistry in a Lake Superior river watershed. Aquat Sci. 68: 40-51.

Futter, M.N. 2007. Modeling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. Water Resour Res. 43: W02424.

Gennings, C., L.A. Molot, and P.J. Dillon. 2001. Enhanced photochemical loss of organic carbon in acidic waters. Biogeochemistry 52: 339-354.

Gergel SE, T.M., Kratz TK 1999. Dissolved Organic Carbon As An Indicator Of The Scale Of Watershed Influence On Lakes And Rivers. Ecoll Appl.9: 1377-1390.

Goldstone, J.V., M. J. Pullin, S. Bertilsson, and B. M. Voelker. 2002. Reactions of hydroxyl radical with humic substances: bleaching, mineralization, and production of bioavailable carbon substrates. Environ. Sci. Tech. 36: 364-372.

Gorham, E., Underwood JK, Janssens JA, Freedman B, Maass W, Waller DH, Ogden JG 1998. The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands. Wetlands 18 (1): 115-132.

Guthery, F.S., J.J. Lusk, and M.J. Peterson. 2001. The fall of the null hypothesis: Liabilities and opportunities. J Wildlife Manage. 65: 379-384.

Häder, D.-P., H. D. Kumar, Ray C. Smith and Robert C. Worrest. 2003. Aquatic ecosystems: effects of solar ultraviolet radiation and interactions with other climatic change factors. Photochem. Photobiol. Sci. 2: 39-50.

Hagedorn, F., K. Kaiser, H. Feyen, and P. Schleppi. 2000. Effects of redox conditions and flow processes on the mobility of dissolved organic carbon and nitrogen in a forest soil. J Environ Qual. 29 (1): 288-297.

Hargreaves, B.R. 2003. Water column optics and penetration of ultraviolet radiation. . In: E.W. Helbling, H. Zagarese, D. Häder and G. Jori (eds), Ultraviolet effects in aquatic organisms and ecosystems: pp59-105.

Haye JM, Santschi PH, Roberts KA, Ray S (2006) Protective role of alginic acid against metal uptake by American oyster (Crassostrea virginica). Environ Chem 3:172–183.

Hillman, G.R., J.C. Feng, C.C. Feng, and Y.H. Wang. 2004. Effects of catchment characteristics and disturbances on storage and export of dissolved organic carbon in a boreal headwater stream. Can J Fisheries and Aquat Sci. 61: 1447-1460.

Hinton, M.J., S.L. Schiff, and M.C. English. 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochemistry 36: 67-88.

Hobbie, J.E. 1992. Microbial control of dissolved organic carbon in lakes: research for the future. Hydrobiologia 229: 169-180.

Hongve, D., O.K. Skogheim, A. Hindar, and H. Abrahamsen. 1980. Effects of heavy metals in combination with nitrilo tri acetic-acid humic-acid and suspended sediment on natural phyto plankton photosynthesis. B Environ Contam Tox. 25: 594-600.

Hongve, D., G. Riise, and J.F. Kristiansen. 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water – a result of increased precipitation? Aquat Sci. 66: 231-238.

Hope, D., M.F. Billett, and M.S. Cresser. 1994. A review of the export of carbon in river water: Fluxes and processes. Environ Pollut. 84: 301-324.

Hudson, J.J., P.J. Dillon, and K.M. Somers. 2003. Long-term patterns in dissolved organic carbon in boreal lakes: the role of incident radiation, precipitation, air temperature, southern oscillation and acid deposition. Hydrol Earth Syst Sc. 7: 390-398.

Hurrell, J.W. 1995. Decadal trends in the North-Atlantic oscillation-regional temperatures and precipitation. Science 269: 676-679.

Jeffries, D., and R. Semkin. 1982. Basin description and information pertinent to mass balance studies of the Turkey Lakes Watershed. TLW-82-01.

Jeffries, D.S., T.A. Clair, S. Couture, P.J. Dillon, J. Dupont, W. Keller, D.K. McNicol, M.A. Turner, R. Vet, and R. Weeber. 2003. Assessing the recovery of lakes in southeastern Canada from the effects of acidic deposition. Ambio 32: 176-182.

Jones, R.I. 1992. The influence of humic substances on lacustrine planktonic food chains. Hydrobiologia 229: 73-91.

Jones, T.H., L.J. Thompson, J.H. Lawton, T.M. Bezemer, R.D. Bardgett, T.M. Blackburn, K.D. Bruce, P.F. Cannon, G.S. Hall, S.E. Hartley, G. Howson, C.G. Jones, C. Kampichler, E. Kandeler, and D.A. Ritchie. 1998. Impacts of rising atmospheric carbon dioxide on model terrestrial ecosystems. Science Wash. 280: 441-443.

Keller, W., J. Heneberry, and J. Leduc. 2005. Linkages between weather, dissolved organic carbon, and cold-water habitat in a Boreal Shield lake recovering from acidification. Can J Fisheries and Aquat Sci. 62:341-347.

Kortelainen, P. 1993. Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics. Can J Fisheries and Aquat Sci. 50: 1477-1483.

Leenheer, J.A., and J.P. Croue. 2003. Characterising aquatic dissolved organic matter. Environ. Sci. Tech. 37: 18A-26A.

Lafleur, P. M. 1993. Potential water balance response to climatic warming: The case of a coastal wetland ecosystem of the James Bay lowland. Wetlands 13: 270-276.

Lennon, J.T. 2004. Experimental evidence that terrestrial carbon subsidies increase CO2 flux from lake ecosystems. Oecologia 138 (4): 584-591.

Lennon, J.T., and L.E. Pfaff. 2005. Source and supply of terrestrial organic matter affects aquatic microbial metabolism. Aquatic Microbial Ecology 39:107-119.

Lofgren, B.M., Quinn, F.H., Clites, A.H., Assel, R.A., Eberhardt, A.J., and Luukkonen, C.L. 2002. Evaluation of potential impacts on Great Lakes water resources based on climate scenarios of two GCMs. J. Gt. Lakes Res. **28**: 537–554.

Magnuson, J.J., B.J. Benson, and T.K. Kratz. 1990. Temporal coherence in the limnology of a suite of lakes in Wisconsin, U.S.A. Freshwater Biology 23:145-159.

Magnuson, J.J., Robertson, D.M., Benson, B.J., Wynne, R.H., Livingstone, D.M., Arai, T., Assel, R.A., Barry, R.G., Card, V., Kuusisto, E., Granin, N.G., Prowse, T.D., Stewart, K.M., Vuglinski, V.S., et al. 2000. Historical trends in lake and river ice cover in the Northern Hemisphere. Science (Wash., D.C.), **289**: 1743–1746.

Malcolm, R.L. 1990. The uniqueness of humic substances in each of soil, stream and marine environments. Anal. Chem. Acta. 232:19-30.

Maloney, K.O., D.P. Morris, C.O. Moses, and C.L. Osburn. 2005. The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. Biogeochemistry 75: 393-407.

Mattsson, T., P. Kortelainen, and A. Raike. 2005. Export of DOM from boreal catchments: impacts of land use cover and climate. Biogeochemistry 76: 373-394.

Mcknight, D.M., and G.R. Aiken. 1998. Scoures and age of aquatic humic. In: D.O.Hessen, L.J.Tranvik (Eds). Aquatic Humic Substances: Ecology and Biogeochemistry. Springer, New York, pp:9-39.

Meyer, E.I., and R. Poepperl. 2004. Assessing food-web structure, matter fluxes, and system attributes of a Central European mountain stream by performing mass-balanced network analysis. Can J Fisheries and Aquat Sci. 61: 1565-1581.

McKenzie, R.L., L.O. Bjorn, A. Bais, and M. Ilyasd. 2003. Changes in biologically active ultraviolet radiation reaching the Earth's surface. Photoch Photobio Sci. 2: 5-15.

Michalzik, B., E. Tipping, J. Mulder, J.F.G. Lancho, E. Matzner, C.L. Bryant, N. Clarke, S. Lofts, and M.A.V. Esteban. 2003. Modelling the production and transport of dissolved organic carbon in forest soils. Biogeochemistry 66: 241-264.

Mierle, G., and R. Ingram. 1991. The role of humic substances in the mobilization of mercury from watersheds. Water Air Soil Poll. 56: 349-357.

Miller, W.L. 1998. Effect of UV Radiation on Aquatic Humus: Photochemical Principles and Experimental Considerations. In: D.O. Hessen, L.J. Tranvik (Eds), Aquatic humic substances: Ecology and Biogeochemistry (page 125-141). Springer, Berlin.

Miller, W.L., and R.G. Zepp. 1995. Photochemical Production of Dissolved Inorganic Carbon from Terrestrial Organic-Matter - Significance to the Oceanic Organic-Carbon Cycle. Geophys Res Lett. 22: 417-420.

Moran, M.A., and R.G. Zepp. 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnol. Oceanogr. 42:1307-1316.

Moeller, R.E. 1994. Contribution of ultraviolet radiation (UV-A, UV-B) to photoinhibition of epilimnetic phytoplankton in lakes of differing UV transparency. Ergeb. Limnol. 43:157–170.

Molot, L.A., and P.J. Dillon. 1997. Photolytic regulation of dissolved organic carbon in northern lakes. Global Biogeochem Cy. 11(3): 357-365.

Molot, L.A., W. Keller, P.R. Leavitt, R.D. Robarts, M.J. Waiser, M.T. Arts, T.A. Clair, R. Pienitz, N.D. Yan, D.K. McNicol, Y.T. Prairie, P.J. Dillon, M. Macrae, R. Bello, R.N. Nordin, P.J. Curtis, J.P. Smol, and M.S.V. Douglas. 2004. Risk analysis of dissolved organic matter-mediated ultraviolet B exposure in Canadian inland waters. Can J Fisheries and Aquat Sci. 61: 2511-2521.

Molot, L.A., J.J. Hudson, P.J. Dillon, and S.A. Miller. 2005. Effect of pH on photo-oxidation of dissolved organic carbon by hydroxyl radicals in a coloured, softwater stream. Aquat Sci. 67: 189-195.

Mopper, K., X. Zhou, R.J. Kieber, D.J. Kieber, R.J. Sikorski, and R.D. Jones. 1991. Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. Nature 353: 60-62.

Moore, T.R. 1998. Dissolved organic carbon: Source, Sinks, and fluxes and role in the soil carbon cycle. In: R. Lal., Soil processes and the carbon cycle, CRC press p281.

Morris, D.P., H. Zagarese, C.E. Williamson, E.G. Balseiro, B.R. Hargreaves, B. Modenutti, R. Moeller, and C. Queimalinos. 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. Limnol. Oceanogr. 40: 1381-1391.

Morris, D.P., H. Zagarese, C.E. Williamson, E.G. Balseiro, B.R. Hargreaves, B. Modenutti, R. Moeller, and C. Queimalinos. 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. Limnol. Oceanogr. 40:1381-1391.

Nagaraja Rao, C.R. 1984. Photosynthetically Active Components of Global Solar Radiation: Measurements and Model Computations. Arch. Met. Geoph. Biocl., Ser. B 34: 353-364.

Osburn, C.L., and D.P. Morris. 2003. Photochemistry of chromophoric dissolved organic matter in natural waters. In: E.W. Helbling, H. Zagarese, D. Häder and

G. Jori (eds), Ultraviolet effects in aquatic organisms and ecosystems. The Royal Society of Chemistry, Cambridge, pp:185-217.

Perdue, E.M. 1998. Chemical composition, structure, and metal binding properties, p. 41-62. In D.O. Hessen and L.J.Tranvik (eds), Aquatic humic substances: Ecology and biogeochemistry. Springer-Verlag.

Perez-Fuentetaja, A., P.J. Dillon, N.D. Yan, and D.J. McQueen. 1999. Significance of dissolved organic carbon in the prediction of thermocline depth in small Canadian shield lakes. Aquat Ecol. 33:127-133.

Rautio, M., Atte Korhola 2002. Effects of ultraviolet radiation and dissolved organic carbon on the survival of subarctic zooplankton. Polar Biology 25:460-468.

Reche, I., M.L. Pace, and J.J. Cole. 2000. Modeled Effects of dissolved organic carbon and solar spectra on photobleaching in Lake ecosystems. Ecosystems 3:419-432.

Reche, I., Pace, M.L. 2002. Linking dynamics of dissolved organic carbon in a forested lake with environmental factors. Biogeochemistry 61:21-36.

Schiff, S., R. Aravena, E. Mewhinney, R. Elgood, B. Warner, P. Dillon, and S. Trumbore. 1998. Precambrian shield wetlands: hydrologic control of the sources and export of dissolved organic matter. Climatic Change 40:167-188.

Schindler, D.W., S.E. Bayley, P.J. Curtis, B.R. Parker, M.P. Stainton, and C.A. Kelly. 1992. Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in Precambrian Shield lakes. Hydrobiologia 229:1-21.

Schindler, D.W., P.J. Curtis, S.E. Bayley, B.R. Parker, K.G. Beaty, and M.P. Stainton. 1997. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochemistry. 36:9-28.

Schindler, D.W., S.E. Bayley, B.R. Parker, K.G. Beaty, D.R. Cruikshank, E.J. Fee, E.U. Schindler, and M.P. Stainton. 1996. The effects of climatic warming on the properties of boreal lakes and streams at the Experimental Lakes Area, northwestern Ontario. Limnol. Oceanogr. 41:1004-1017.

Scully, N.M., and D.R.S. Lean. 1994. The attenuation of ultraviolet radiation in temperate lakes. Advances in Limnology. 45:135-144.

Semkin, R., and D. Jeffries. 1983. Rock chemistry in the Turkey Lakes Watershed. TLW-83-03.

Shaw, P.J., R.I. Jones, and H. De Haan. 2000. The influence of humic substances on the molecular weight distributions of phosphate and iron in epilimnetic lake waters. Freshwater Biol. 45:383-393.

Shiller, A.M., S.W. Duan, E.P. van, and T.S. Bianchi. 2006. Photo-oxidation of dissolved organic matter in river water and its effect on trace element speciation Limnol. Oceanogr. 51 (4):1716-1728.

Spitzy, A., and J. Leenheer. 1991. Dissolved organic carbon in rivers. In: R.F.C. Mantoura, J.M. Martin and R. Wollast, Biogeochemistry of major world rivers. John Wiley & Sons Ltd, New York. pp 213-232.

Sobek, S., L.J. Tranvik, Y.T. Prairie, P. Kortelainen, and J.J. Cole. 2007. Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. Limnol. Oceanogr. 52(3):1208-1219.

Steinberg, C., A. Paul, S. Pflugmacher, T. Meinelt, R. Klocking, and C. Wiegand. 2003. Pure humic substances have the potential to act as xenobiotic chemicals - A review. Fresen Environ Bull. 12 (5): 391-401 2003.

Stenseth, N.C., Geir Ottersen, James W. Hurrell, Atle Mysterud,, and K.-S.C. Mauricio Lima, Nigel G. Yoccoz and BjørnAÊ dlandsvik. 2003. Studying climate effects on ecology through the use of climate indices: the North Atlantic Oscillation, El Niño Southern Oscillation and beyond. Proc. R. Soc. Lond. B 270:2087-2096.

Sun, L., and E.M. Perdue. 1997. Use of elemental composition to predict bioavailability of dissolved organic matter in a Georgia river Lmnol. Oceanogr. (42): 714-721.

Sunda, W.G. 1995. The inlfuence of nonliving organic matter on the availability and cycling of plant nutrients in seawater. In: R.G. Zepp and C.H. Sountag (Eds), Role of non-living Organic Matter in the Earth's Carbon Cycle. Wiley, New York, pp:191-207.

Snucins, E., and J. Gunn. 2000. Interannual variation in the thermal structure of clear and colored lakes. Limnol. Oceanogr. 45(7):1647-1654.

Thurman, E.M. 1985. Organic Geochemistry of Natural Waters E. M. Thurman. Martinus Nijhoff/Dr. W. Junk Publishers. pp 497

Tzortziou, M., Osburn CL, Christopher L., Neale PJ 2007. Photobleaching of dissolved organic material from a tidal marsh-estuarine system of the Chesapeake Bay. Photochem Photobiol. 83 (4):782-792.

Wetzel, R.G., and A.K. Ward. 1992. Primary production, p. 354-369, *In* P. Calow and G. E. Petts, eds. Rivers Handbook, 1st ed. Blackwell Scientific, Oxford.

Wetzel, R.G., P.G. Hatcher, and T.S. Bianchi. 1995. Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism. Limnol. Oceanogr. 40:1369-1380.

Wetzel, R.G. 2001. Limnology : lake and river ecosystems. 3rd ed. Academic Press, San Diego.

Wetzel, G.R. 2003. Dissolved Organic Carbon: Detrital Energetics, Metabolic Regulators, and Drivers of Ecosystem Stability of Aquatic Ecosystems, p. 455 - 477, *In* C. S. Findlay and R. L. Sinsabaugh, eds. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Academic Press, San Diego, California

Williamson, C.E., H.E. Zagarese, P.C. Schulze, B.R. Hargreaves, and J. Seva. 1994. The impact of short-term exposure to UV-b radiation on zooplankton communities in north temperate lakes. J Plankton Res. 16 (3):205-218.

Williamson, C.E., R.S. Stemberger, D.P. Morris, T.M. Frost, and S.G. Paulsen. 1996. Ultraviolet radiation in North American lakes: Attenuation estimates from DOC measurements and implications for plankton communities. Limnol. Oceanogr. 41:1024-1034.

Williamson, C.E., D.P. Morris, M.L. Pace, and O.G. Olson. 1999. Dissolved organic carbon and nutrients as regulators of lake ecosystems: resurrection of a more integrated paradigm. Limnol. Oceanogr. 44(3, part ii):795-803.

Witters, H.E., S.V. Puymbroeck, J.H.D. Vangenechten, and O.L.J. Vanderborght. 1990. The effect of humic substances on the toxicity of aluminum to adult rainbow trout oncorhynchus-mykiss walbaum. J Fish Biol. 37: 43-54

Appendix 1. Characteristics of the 56 study lakes from 5 sites across Eastern Canada. DOC concentration and pH were estimated from whole lake samples taken during the ice-free period, except for Kejimkujik and Yarmouth, where DOC and pH measurements were taken at spring and fall lake turnover. The periods of study for each site were: Dorset 1978 -1998; Turkey Lakes Watershed 1982 - 2002; Experimental Lake Area 1982 - 2002; and Kejimkujik and Yarmouth 1982 - 2002. The average lake area (Ao), maximum depth (Zmax), mean depth (Zm), pH and DOC concentration for each lake in each site is also listed below.

Region	Lake	Latitude	Longitude	Ao (ha)	Zmax (m)	Zm (m)	pH	DOC (mg l^{-1})
Dorset	Blue Chalk	45°12'	78°56'	52.4	23.0	8.5	6.63	1.8
	Chub	45°13'	78°59'	34.4	27.0	8.9	5.62	4.8
	Crosson	45°05'	79°02'	56.7	25.0	9.2	5.57	4.2
	Dickie	45°09'	79°05'	93.6	12.0	5	5.87	5.1
	Harp	45°23'	79°07'	71.4	37.5	13.3	6.26	3.8
	Heney	45°08'	79°06'	21.4	5.8	3.3	5.88	3.0
	Plastic	45°11'	78°50'	32.1	16.3	7.9	5.75	2.2
	Red Chalk	45°11'	78°56'	57.1	38.0	14.2	6.29	2.6
	Average			52.4	21.6	8.8	6.0	3.4

Appendix 1. (Continued)

Region	Lake	Latitude	Longitude	Ao (ha)	Zmax (m)	Zm (m)	pH	DOC (mg l^{-1})
ELA	Lake 224	49°69’	93°72’	25.9	27	11.6	6.6	3.0
	Lake 239	49°39’	93°43’	54.3	30	10.9	7.0	6.6
	Lake 240	49°39’	93°43’	44.2	13	6.0	7.17	6.7
	Lake 373	49°44’	93°47’	27.6	21.5	11.3	7.33	3.9
	Average			38.5	22.9	10.0	7.0	5.0
TLW	Batchawana N	47°04	84°23	5.9	11.3	3.9	6.04	4.1
	Batchawana S	47°03	84°23	5.8	10.9	3.3	6.0	4.8
	Wishart	47°03	84°23	19.2	4.5	2.2	---	4.5
	Little Turkey	47°02	84°24	19.2	13.0	6.0	6.86	4.0
	Turkey	47°02	84°25	52.0	37.0	12.2	6.7	3.6
	Average			20.4	15.3	5.5	6.4	4.2

Appendix 1. (Continued)

Region	Lake	Latitude	Longitude	Ao (ha)	Zmax (m)	Zm (m)	pH	DOC (mg l^{-1})
Kejimkujik	Back	44°17'	65°16'	64.9	5.8	2.2	5.4	3.6
	Beaverskin	44°18'	65°19'	39.5	6.3	2.2	5.4	2.1
	Ben	44°20'	65°19'	20.4	0.7	0.5	4.6	4.8
	Big Dam East	44°27'	65°17'	45.5	---	---	6.0	3.4
	Big Dam West	44°27'	65°17'	105.4	9.5	2.5	5.0	9.8
	Big Red	44°20'	65°22'	70.5	2.2	1.0	4.3	15.8
	Channel	44°25'	65°18'	68.4	1.8	1.1	4.8	10.9
	Cobielle	44°19'	65°13'	131.8	6.3	2.0	5.4	2.7
	Frozen Ocean	44°27'	65°20'	228.0	7.6	1.9	4.9	10.2
	Georege kejimkujik	---	---	---	---	---	5.0	6.9
	Grafton	44°23'	65°10'	270.4	10.0	2.8	5.9	4.9
	High	44°21'	65°15'	3.8	2.8	1.5	5.0	9.6
	Kejimkujik	44°23'	65°15'	264.3	19.2	4.4	5.0	7.0
	Liberty	44°23'	65°25'	73.4	---	---	5.3	4.5

Appendix 1. (Continued)

Region	Lake	Latitude	Longitude	Ao (ha)	Zmax (m)	Zm (m)	pH	DOC (mg l^{-1})
Kejimkujik	Little Red	44°22'	65°23'	19.6	1.3	0.7	4.4	15.4
	Loon	---	---	---	---	---	5.1	6.6
	Luxton	44°22'	65°20'	47.1	8.5	3.0	4.8	6.8
	McGinty	44°21'	65°09'	4.4	4.0	1.4	6.1	7.7
	Mountain	47'50'	55'07'	580.0	---	---	5.3	3.4
	Mttom	44°22'	65°21'	14.0	---	---	4.7	8.6
	Mud	44°16'	65°13'	7.0	2.2	1.0	4.9	8.9
	Pebble	44°18'	65°21'	33.4	2.5	1.4	4.5	10.1
	Peskawa	44°19'	65°21'	388.5	9.0	3.2	4.7	7.1
	Peskowesk	44°19'	65°16'	685.0	13.0	3.9	4.9	5.3
	Poplar	44°21'	65°26'	84.0	---	---	4.8	5.9
	Snake	44°21'	65°12'	12.7	2.5	1.4	4.8	12.8
	Upper Silver	44°16'	65°14'	24.3	5.8	2.3	5.9	3.0
	Average			135.0	6.0	2.0	5.1	7.3

Appendix 1. (Continued)

Region	Lake	Latitude	Longitude	Ao (ha)	Zmax (m)	Zm (m)	pH	DOC (mg l^{-1})
Yarmouth	Bird	43°58'	65°56'	30.0	---	---	6.5	2.7
	Brenton	43°57'	66°04'	58.4	3.7	1.2	5.0	16.2
	Cedar	44°01'	66°06'	100.0	---	---	6.3	5.3
	George	---	---	---	---	---	5.8	3.2
	Jesse	44°01'	66°00'	26.8	5.7	2.4	6.1	4.3
	Killams	44°00'	66°04'	14.8	1.5	0.7	6.0	3.6
	Lower Corning	44°03'	66°04'	82.1	3.8	1.4	5.9	5.2
	Pierce	44°07'	66°05'	37.2	4.2	1.9	5.8	4.3
	Snare	44°06'	65°58'	64.7	6.7	1.3	4.8	9.3
	Tedford	44°05'	66°00'	81.6	4.3	1.2	6.3	2.7
	Trefrey	43°50'	66°02'	29.6	12.4	3.1	6.4	5.7
	Average			93.8	5.7	1.9	5.5	6.85