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Dissolved Organic Matter in Subarctic Streams and Rivers: Direct and Proxy Measures of Quantity, Quality, and Mercury

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Graduate Program in Geology

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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Abstract

The drainage network of the Hudson Bay Lowlands (HBL) peatland complex regulates the transport of freshwater and solutes, including dissolved organic matter (DOM) and mercury, to Hudson Bay. Due to the remoteness and areal extent of the HBL, traditional, campaign-based sampling programs are unable to fully elucidate the region’s hydrology and biogeochemistry. This study investigated seasonal variability of DOM quantity and quality in two distinct stream orders to explore DOM sources to surface waters in the region, and assessed optical measurements as proxies for riverine DOM and mercury. In-stream primary production and enhanced microbial processing influenced DOM characteristics during base flow and negatively impacted mercury-DOM relationships in the higher order river. These autochthonous DOM sources reflected in-stream processes and not peatland-derived carbon, as were characteristic of the lower order stream. Optical measurements varied in their effectiveness as proxies depending on DOM source (e.g., groundwater and primary production) and concentration (peat-dominated streams).

Keywords

Hudson Bay Lowlands, Peatland, Dissolved Organic Matter (DOM), Mercury, In Situ Proxy, Spectroscopy, Fluorescence, Absorbance, Hydrological Connectivity, Spatial Variability, Seasonal Variability, Subarctic Rivers
Co-Authorship Statement

I hereby declare that I am the sole author of this thesis, except as noted (below). I understand that my thesis may be made electronically available to the public.

Exceptions to sole authorship:

For all chapters in this thesis, Dr. Brian Branfireun acted as an advisor, editor, and offered suggestions on scientific content, and the treatment and presentation of data. He will be listed as a co-author on any subsequent publications stemming from this work.
Dedication

This thesis is dedicated to my loving family: my parents, Maureen and Paul, my sister, Laura, and my partner in life, Tom.

Thank you for your unwavering support.
Acknowledgments

There have been countless individuals who have influenced the development and completion of this thesis. At this time, I would like to take the opportunity to thank them for their contributions and for their support during this process.

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<tr>
<td>%o</td>
<td>Permille</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>°N</td>
<td>Degrees North</td>
</tr>
<tr>
<td>°W</td>
<td>Degrees West</td>
</tr>
<tr>
<td>18O</td>
<td>Oxygen-18 isotope</td>
</tr>
<tr>
<td>A254</td>
<td>Absorbance at Measured at Wavelength 254 nm</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
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<tr>
<td>ca.</td>
<td>Circa (approximately)</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Calcium Ion</td>
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<tr>
<td>CDOM</td>
<td>Chromophoric Dissolved Organic Matter</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Chloride Ion</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeters</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CRDS</td>
<td>Cavity Ring-Down Spectroscopy</td>
</tr>
<tr>
<td>CVAFS</td>
<td>Cold-Vapor Atomic Fluorescence Spectroscopy</td>
</tr>
<tr>
<td>D or ²H</td>
<td>Deuterium Isotope</td>
</tr>
<tr>
<td>Da</td>
<td>Daltons</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized (Water)</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
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<td>EEM</td>
<td>Excitation-Emission Matrix</td>
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<td>Em</td>
<td>Emission Wavelength (nm)</td>
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<td>Evapotranspiration</td>
</tr>
<tr>
<td>Ex</td>
<td>Excitation Wavelength (nm)</td>
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<td>FDOM</td>
<td>Fluorescent Chromophoric Dissolved Organic Matter</td>
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<tr>
<td>FI</td>
<td>Fluorescence Index</td>
</tr>
<tr>
<td>FWT</td>
<td>Fen Water Track</td>
</tr>
<tr>
<td>Gi</td>
<td>Groundwater Inputs</td>
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<tr>
<td>GMWL</td>
<td>Global Meteoric Water Line</td>
</tr>
<tr>
<td>Go</td>
<td>Groundwater Outputs</td>
</tr>
<tr>
<td>Gt</td>
<td>Gigatons</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>HBL</td>
<td>Hudson Bay Lowlands</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-Density Polyethylene</td>
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<tr>
<td>Hg</td>
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<td>Humification Index</td>
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<td>Hertz</td>
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<td>Inner-Filter Effects</td>
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<tr>
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<td>James Bay Lowland</td>
</tr>
<tr>
<td>K</td>
<td>Hydraulic Conductivity</td>
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<tr>
<td>km</td>
<td>Kilometers</td>
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<td>KMO</td>
<td>Kaiser-Meyer-Olkin</td>
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<tr>
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<tr>
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<td>Local Meteoric Water Line</td>
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<td>Meters</td>
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<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>MDL</td>
<td>Method Detection Limit</td>
</tr>
<tr>
<td>MeHg</td>
<td>Methylmercury</td>
</tr>
<tr>
<td>mg</td>
<td>Milligrams</td>
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<tr>
<td>Mg$^{2+}$</td>
<td>Magnesium Ion</td>
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<tr>
<td>mL</td>
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<td>Method Reporting Limit</td>
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<td>NGC</td>
<td>North Granny Creek</td>
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<td>Nayshkootayaow River</td>
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<tr>
<td>OM</td>
<td>Organic Matter</td>
</tr>
<tr>
<td>P</td>
<td>Precipitation</td>
</tr>
<tr>
<td>PAR</td>
<td>Photosynthetically Active Radiation</td>
</tr>
<tr>
<td>PARAFAC</td>
<td>Parallel Factor (Analysis)</td>
</tr>
<tr>
<td>PC</td>
<td>Principal Component</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>PETG</td>
<td>Polyethylene Terephthalate Glycol-Modified</td>
</tr>
<tr>
<td>Pg</td>
<td>Petagrams</td>
</tr>
<tr>
<td>pH</td>
<td>Potential of hydrogen</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
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<tr>
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<td>Definition</td>
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<tr>
<td>QA/QC</td>
<td>Quality Assurance and Quality Control</td>
</tr>
<tr>
<td>QSE</td>
<td>Quinine Sulfate Equivalents</td>
</tr>
<tr>
<td>r.t.s</td>
<td>Relative to Peat Surface</td>
</tr>
<tr>
<td>R.U.</td>
<td>Raman Units</td>
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<tr>
<td>S</td>
<td>Storage</td>
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<td>s</td>
<td>Second</td>
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<td>SC</td>
<td>Specific Conductivity</td>
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<td>SD</td>
<td>Standard Deviation</td>
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<td>spp.</td>
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<td>THg</td>
<td>Total Mercury</td>
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<td>TOC</td>
<td>Total Organic Carbon</td>
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<td>UV</td>
<td>Ultraviolet</td>
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<td>V</td>
<td>Volts</td>
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<td>Vis</td>
<td>Visible</td>
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<tr>
<td>VSMOW</td>
<td>Vienna Standard Mean Ocean Water</td>
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<td>δ¹⁸O</td>
<td>Delta-O-18; Stable Oxygen Isotope Ratio of $^{18}$O:$^{16}$O</td>
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<td>Delta-D; Stable Hydrogen Isotope Ratio of $^2$H:H</td>
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<tr>
<td>μg</td>
<td>Micrograms</td>
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<td>μS</td>
<td>Microsiemens</td>
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CHAPTER 1

1 Literature Review and Introduction

1.1 Northern Peatlands: Forms and Functions

1.1.1 Peatland Landforms

Wetlands cover 5-8% of the Earth, and 14% of Canada’s land surface (NWWG, 1988; Mitsch and Gosselink, 2007). They are among the world’s most important ecosystems, serving as a unique habitat for a diversity of flora and fauna, as well as providing an array of benefits to society, including flood moderation, improvements to water quality, food production, recreation, and ecotourism (Mitra et al., 2005; Mitsch and Gosselink, 2007). Wetlands also sequester large amounts of carbon (C), estimated at roughly 20% of the total global terrestrial store (Roulet, 2000). The Canadian Wetland Classification System defines a wetland as “land that is saturated with water long enough to promote wetland or aquatic processes as indicated by poorly drained soils, hydrophytic vegetation and various kinds of biological activity which are adapted to a wet environment” (NWWG, 1997). Wetlands can be separated into two major categories: organic and mineral. Organic wetlands, also known as peatlands, are wetlands where partially decayed organic matter (OM) has accumulated beyond a depth of 40 cm in the form of peat, typically in regions with relatively flat topography, cold climates, and poor drainage (Gorham, 1991; NWWG, 1997).

Peatlands constitute only 3% of global land area, the majority of which are located in boreal and subarctic regions at latitudes between 50° and 70° N (Matthews and Fung, 1987; Tarnocai, 2006). Northern peatlands act as a substantial long-term C sink, where the rate of net primary productivity, although quite slow, has outpaced the rate of OM decomposition for millennia, resulting in the net accumulation of between 270 to 370 Pg C (Gorham, 1991; Turunen et al., 2002), or roughly 30-50% of the carbon dioxide (CO₂) currently held in the atmosphere (Limpens et al., 2008). The dense layer of OM in peatlands also exerts a strong influence on the chemistry of peatland-derived surface waters, runoff, and shallow subsurface flows. The largest contiguous peatland expanses are located in the West Siberian Plain in Russia and the Hudson Bay Lowlands (HBL) of Canada. These vast peatland complexes lie on flat landscapes and are underlain by relatively impermeable soils, thus promoting waterlogging and anaerobic conditions (Gorham, 1991), creating an ideal reducing
environment for mercury (Hg) methylation. Despite the importance of these areas to global biogeochemical cycles (mainly carbon), much of the current knowledge of peatland hydrology and biogeochemistry originates from less sizeable peatlands, notably the patterned peatlands of Minnesota (see Wright et al., 1992), or more isolated systems in Canada (e.g., Price et al., 2005; Waddington et al., 2009).

Among the different classes of peatlands are bogs and fens, which are distinguished principally by their hydrology, vegetation assemblages, and biogeochemistry. Bogs are ombrogenous since precipitation is the only input of water to the system, whereas fens are minerogenous because they also receive additional hydrological inputs of groundwater (and associated solutes) from adjacent landforms and underlying mineral strata (NWWG, 1997). Bogs are raised landforms relative to the surrounding landscape, often characterized by a rounded, domed shape, and a water table that follows closely to the topography. The high rates of peat accumulation in bogs result in deep peat deposits, which in turn lead to a disconnect between the bog’s surficial peat and the mineral-rich groundwaters beneath (Ingram, 1983). The vegetation in bogs consists primarily of Sphagnum species of moss, ericaceous shrubs (e.g., Chamaedaphne calyculata, Rhododendron spp.), and lichens (Cladonia spp.), while the bog itself may be either sparsely forested by stunted black spruce (Picea mariana), or treeless (NWWG, 1997). Bog surface pore waters are mineral-poor and acidic in nature, generally ranging between pH 4.0 and 4.8 as a result of the predominance of mildly acidic precipitation inputs, a low buffering capacity, and the secretion of organic acids by live and decomposing Sphagnum spp. (Clymo, 1964; NWWG, 1997).

In fen peatlands, pore waters are less acidic (pH > 4.6), and contain higher concentrations of base cations (i.e., Ca$^{2+}$, Mg$^{2+}$, and K$^+$) than bogs, due to inputs of groundwater laden with solutes (Siegel and Glaser, 2006). Fens are also generally wetter than bogs and have greater vegetation diversity as a result of a shallower water table and the enhanced degree of groundwater connection. Vegetation is usually dominated by herbaceous species (mostly sedges; Cyperaceae spp.), brown mosses (Amblystegiaceae spp.), and depending on the mineral richness of the fen, stunted tamarack (Larix laricina). The assemblage of vascular plant species in fens also enhances oxygenation in the surface peat through root aeration, and fuels higher rates of decomposition (D’Andrilli et al., 2010).
In peatlands, a widely accepted and commonly employed simplistic model of peat profile structure distinguishes two-layers, termed the ‘acrotelm’ and ‘catotelm’. The acrotelm typically occupies the upper, more porous 0-50 cm of peat, encompassing the active aerobic zone of relatively high hydraulic conductivity ($K = 10^{-2}$ to $10^{-6}$ m s$^{-1}$), and rates of production that exceed the relatively high rates of decomposition (Clymo, 1984; Chason and Siegel, 1986; Holden, 2005). The acrotelm is also sensitive to fluctuations in the water table, the effects of evapotranspiration, and precipitation inputs (Chason and Siegel, 1986). The lower catotelm layer, much thicker than the acrotelm (up to several meters deep), is an anaerobic zone of permanent saturation (by definition) in which water movement is more restricted. It is characterized by much lower rates of decomposition as well as lower hydraulic conductivity ($K = 10^{-5}$ to $10^{-9}$ m s$^{-1}$) and porosity (<85%), which decrease with depth and degree of humification (i.e., the decomposition and transformation of OM into more complex and refractory humic substances) (Clymo, 1984; Chason and Siegel, 1986). The acrotelm-catotelm model provides a basic but effective conceptualization for understanding the hydrology and ecology of peatlands, however it has recently been scrutinized for its inability to account for hydrological and biogeochemical complexity in peatlands, such as water table fluctuations, horizontal spatial heterogeneity, and biogeochemical hot spots (Holden, 2005; Morris et al., 2011).

1.1.2 Hydrology and Hydrological Connectivity

Hydrology governs peatland initiation, development, and chemistry (Mitsch and Gosselink, 2007). Peatlands form when the annual hydrological inputs exceed hydrological outputs, and there is a positive change in storage ($S$) in the generalized water balance of a peatland (Equation 1):

$$\Delta S = P + S_i + G_i - ET - S_o - G_o$$

Equation 1

Where P is precipitation, $S_i$ is surface water inputs, $G_i$ is groundwater inputs, ET is evapotranspiration, $S_o$ is surface water outputs, and $G_o$ is groundwater outputs.

While the water balance equation applies in full to fen peatlands, the water balance in bogs (Equation 2) is more simplistic due to their ombrogenous nature:
\[ \Delta S = P - ET - S_o - G_o \]  \hspace{1cm} \text{Equation 2}

Precipitation and evapotranspiration are generally considered the biggest gain and loss of water to and from a peatland, respectively. Runoff from peatlands can occur as surface flow (Ivanov, 1981; Ingram, 1982; Ingram, 1983), or as groundwater flow through deeper peats (Siegel and Glaser, 1987). In large patterned fens, characteristic of subarctic peatlands, when the water table exceeds peat surface, surface flows can be directed through a network of ridges and pools that spill into each other, or are connected by channels of preferential flow (NWWG, 1997; Glaser et al., 2004). Generally, the potential for a peatland to store water is significantly increased if the peatland landform (e.g., bog or fen) contains pools. In larger bogs, upwelling groundwater may be deflected to the bog margins and discharged on the surface, creating internal fen-like water tracks that are central in directing drainage through the landform (Glaser et al., 1997; Richardson et al., 2012; Ulanowski and Branfireun, 2014).

When the water table falls below the peat surface (generally during summer months when evapotranspirative losses exceed precipitation inputs), groundwater flows dominate non-atmospheric water losses. Since the vertical hydraulic gradients in large peatland complexes are generally very small (< 0.1), the flow of water through porous media is primarily lateral and is controlled by the hydraulic conductivity of peat. Hydraulic conductivity generally decreases with depth (from \(10^{-2}\) m s\(^{-1}\) at the surface to \(10^{-8}\) m s\(^{-1}\) at depth) (Chason and Siegel, 1986; Reeve et al., 2000), so the majority of water losses occur through the uppermost layer of peat; the magnitude of flow dictated by the position of the water table. Numerical simulations of large peatland complexes have also shown that the vertical exchange of water and solutes between underlying mineral strata is negligible if the hydraulic conductivity of the layer beneath the peat is sufficiently low (< \(10^{-7}\) m s\(^{-1}\)) (Reeve et al., 2000). Furthermore, it has been suggested that dispersion processes resulting from heterogeneities in the peat are primarily responsible for the top-down and bottom-up redistribution of solutes in the peat profile (Reeve et al., 2001). However, empirical field studies in the HBL suggest that smaller-scale flows that result from ponds, ridges, and breaks in topography can also contribute to the complex patterning of pore water solutes often found in bogs and fens (Ulanowski and Branfireun, 2014). Drainage features, such as macropores and soil pipes, can enhance water losses in peatlands as they introduce additional hydrological pathways that are
uncharacteristic of the rest of the peatland and are often difficult to quantify. These are usually located near palsas (permafrost features), bioherms with karst bedrock (Whittington and Price, 2012), or in near-stream riparian areas (Kline and Branfireun, 2014).

The concept of hydrological connectivity relates to the functional connectedness of landscape components and the resulting flow of water, matter (e.g., solutes), and energy from one part of the landscape to another (Bracken and Croke, 2007; Tetzlaff et al., 2007). Connectivity is dynamic and varies as a function of moisture conditions, landscape topography, and the nature, frequency, and distribution of rainfall. Understanding connectivity is integral in predicting the overall streamflow and runoff response within large drainage basins (Phillips et al., 2011). Several tracers have been used in elucidating the spatial and temporal variability of hydrological connectivity, including stable isotopes (δD and δ^{18}O) (Tetzlaff et al., 2014), specific conductivity (Orlova and Branfireun, 2014), and, to a certain degree, dissolved organic matter (DOM) optical properties (Walker et al., 2013).

In large peatland environments, the areal extent and storage dynamics of individual catchment units affect overall hydrological responses and connectivity. Peatlands have the capacity to store substantial amounts of water (Holden, 2005). Peatland streamflow can respond rapidly to rainfall events depending on peatland saturation and storage conditions, such that wetter antecedent moisture conditions facilitate the connection of landscape and runoff units. As peatland connectivity decreases with summer drying, the water table deepens and the amount of available storage within the peatland increases, and larger rain events are needed to trigger a noticeable response or to connect landscape units (Quinton and Roulet, 1998). After prolonged dry periods, each successive rainfall contributes to a rise in the water table, and may deliver increasing streamflow responses, relative to the rainfall (Holden, 2005). Ulanowski and Branfireun (2014) recently suggested that this response to precipitation and peatland hydrological connectivity hinges on satisfying some threshold moisture deficit or water table position in the peatland, otherwise the hydrologic connectivity between landscape units and tributaries is maintained only by diffuse groundwater flow. In northern peatlands, bogs have been characterized as storage areas that reduce runoff, while fen systems, such as channel fens, fen water tracks, and patterned or ribbed fens act as conveyors of flow (Quinton and Roulet, 1998; Richardson et al., 2012; Ulanowski and Branfireun, 2014). Meanwhile, lower order streams are noted to yield less runoff relative to
their catchment areas than higher order streams, due to a greater proportion of the incoming precipitation being evaporated or stored by the peatland (Richardson et al., 2012). Due to greater incision, higher order rivers are prone to a more substantial connection with bedrock groundwater, which comparatively contributes little, if at all, to shallow peatland streams.

Hydrological connectivity changes seasonally in northern peatlands. During the subarctic spring freshet, increases in both temperature and precipitation are accompanied by extensive snowmelt and peak flows. The greatest connectivity typically occurs during this time, as the still-frozen substratum perches flow to the near-surface acrotelm and overland pathways (Carey et al., 2013). Subsurface thaw allows inputs of ‘new’ water to infiltrate to greater peat depths. There is a progressive decrease in connectivity into the summer due to typically drier conditions and lower river flows. Summer base flow is generally sustained by seepage from deep pore waters or groundwater until rainfall events in the late summer and fall increase connectivity of the landscape and drainage network. Macropipe networks in peatlands also enhance subsurface connectivity by providing an additional pathway for the flow of water and solutes between peat and surface waters. These pipe networks, though understudied, have been closely coupled to the peatland stream network (Holden, 2005; Kline and Branfireun, 2014).

1.2 Carbon Cycling in Peatlands

Peatlands have among the highest C densities of any ecosystem and play an important role in global C cycling (Blodau, 2002; Davidson and Janssens, 2006). The net sequestration of C in northern peatlands is determined by the balance of inputs and outputs of C. Inputs are principally from photosynthesis, plant litter production, and root exudation, while outputs consist of the efflux of gaseous CO₂ and methane (CH₄) from the peat surface, root respiration, microbial decomposition, and leaching of dissolved organic carbon (DOC) through macropores (Figure 1.1) (Holden, 2005; Davidson and Janssens, 2006). It has long been recognized that climate change will pose a threat to the stability of C stocks in northern peatlands (Gorham, 1991), due to potential impacts on microbial activity, vegetation structure, and hydrological regimes that control the transport of CO₂, CH₄, and DOC (Trettin et al., 2006; Limpens et al., 2008).
Peatlands serve as both a sink and source of major greenhouse gases. They generally act as a net sink of CO₂, exchanging between 0.1 to 0.5 Pg yr⁻¹ with the atmosphere, and are also responsible for the emission of ~3 to 5% of the global CH₄ burden to the atmosphere (on average, 5 to 80 mg m⁻² d⁻¹) (Blodau, 2002; Frolking et al., 2006; Roulet et al., 2007).

Dissolved organic carbon, the product of incomplete decomposition of OM, is present in relatively high concentrations in northern peatlands, typically within the range of 20 to 80 mg L⁻¹ (Blodau, 2002). In addition to land-atmosphere exchanges, waterborne losses of DOC represent a large export of C from northern peatlands (1 to 50 g m⁻² yr⁻¹) (Dillon and Molot, 1997; Fraser et al., 2001), and a major part of the complete peatland carbon budget. Water table position, water source, and temperature can affect the availability of nutrients and electron acceptors for microbial activity, thus affecting redox potential and OM decomposition (see Mitsch and Gosselink, 2007; Limpens et al., 2008). In northern Canadian peatlands, climate change is expected to increase temperatures above 1985 levels by 3 to 5 ºC by 2020, and translate into a 14 to 22 cm deepening of the water table relative to the peat surface (Roulet et al., 1992; Hengeveld, 2000), however the overall DOC response to these changes is still unclear (Preston et al., 2011). Measurements quantifying the exchange of gaseous C with the atmosphere, such as with chamber or micrometeorological methods, are rarely coupled with thorough measurements of DOC transport (Limpens et al., 2008). Improper quantification of these fluxes, along with the hydrological and biogeochemical complexity of DOC dynamics can lead to inaccurate estimates of a system’s total C budget.
1.2.1 Dissolved Organic Matter

Organic matter is ubiquitous in all natural waters in dissolved, colloidal, and particulate forms. The dissolved fraction of OM, or DOM, the most widely studied form, is operationally defined as the organic material that can pass through a 0.45-μm filter (Thurman, 1985; USEPA, 2009). Dissolved organic matter is a complex heterogeneous mixture of high to low molecular weight organic compounds that vary in terms of their solubility, structure, bioavailability, ecological function, and their optical properties (Leenheer and Croué, 2003; Aiken, 2014). Comprising the dominant proportion of DOM are humic substances, categorized as fulvic and humic acids. Fulvic acids are typically yellow in color, consist of moderate molecular weight (ca. 500 Da) molecules, and are soluble at all pH values. Humic acids are much darker (brown to black) and larger molecules (>100,000 Da), and are soluble above pH 2 (Aiken et al., 1985; McKnight and Aiken, 1998). In natural waters, DOM is commonly classified in reference to its origin, which can be either from biological processes occurring within the aquatic environment (autochthonous) or from
external terrestrial sources (allochthonous). Autochthonous DOM is principally derived from algae and macrophytes, although may originate from other sources, and can be either lightly colored or uncolored (Mostofa et al., 2013). It consists mostly of lower molecular weight (<100 Da) compounds and can include carbohydrates, proteins, amino acids, and organic acids (Bertilsson and Jones, 2003; Mostofa et al., 2013). Meanwhile, allochthonous DOM is derived from the erosion of organic soils/peat and degradation of plant material that is incorporated into runoff (Aitkenhead-Peterson et al., 2003). Allochthonous DOM, a combination of humic substances, is often highly colored and can contain an assortment of functional groups, such as aliphatic, aromatic, and carboxyl groups (Ibid.). The majority of DOM in riverine systems is allochthonous, accounting for 50-75% of the total DOM pool in natural freshwaters, and of 80-90% in wetlands (McKnight et al., 2003). The DOM composition of a typical riverine sample further exemplifies the substantial influence of allochthonous carbon and heterogeneity of DOM (Figure 1.2).

The molecular complexity of DOM results in variations in its characteristics. For instance, bioavailability may change throughout the DOM pool, and is therefore, commonly described as either “labile” or “recalcitrant” in terms of its availability for biological degradation.

Figure 1.2: Pie diagram showing the composition of DOM for a typical river sample; adapted from McKnight et al. (2003).
Labile DOM is thought to constitute only a minor proportion (10-40%) of DOM, and is readily available for microbial decomposition, providing energy for microbial metabolism (Søodergaard and Middelboe, 1995). The remaining proportion of DOM is considered recalcitrant and is mostly resistant to biological degradation (Søodergaard and Middelboe, 1995; Tranvik and Kokalj, 1998). The turnover of OM depends largely on the overall lability of the bulk pool, and can range from minutes to centuries, or even longer, depending on the relative proportions of labile and recalcitrant fractions (Del Giorgio and Davis, 2003). The bioavailability of DOM is determined by a combination of intrinsic (e.g., source, molecular weight, and aromaticity) and extrinsic (e.g., temperature, nutrient and oxygen availability, water stress, and light exposure) factors (Del Giorgio and Davis, 2003). With regard to source, allochthonous DOM is generally considered as the main source of the recalcitrant DOM pool, while autochthonous DOM is more labile (Søodergaard and Middelboe, 1995). However, recent studies suggest that, while autochthonous protein-like molecules play a major role in determining DOM bioavailability, the allochthonous humic-like fraction fuels a slight but constant amount of microbial activity (Guillemette and del Giorgio, 2011). Furthermore, when isolated from fresh inputs over longer timescales (i.e., months to years), allochthonous DOM may become a relatively more important fraction of the available carbon pool since the labile autochthonous fraction is preferentially utilized by bacteria, and is rapidly depleted (Koehler et al., 2012). Over such significant timescales, allochthonous DOM is thought to regulate overall DOM bioavailability in terrestrially influenced rivers and streams (Fellman et al., 2008; Holmes et al., 2008; Balcarczyk et al., 2009; Fellman et al., 2009; Guillemette and del Giorgio, 2011). However, photodegradation is widely reported to alter DOM bioavailability. For instance, allochthonous DOM is particularly sensitive to photodegradation, and exposure to sunlight can result in the breakdown of the otherwise recalcitrant pool of DOM into more labile molecules (see Moran and Covert, 2003).

Aromaticity describes C compounds having a resonance delocalized, cyclic molecular structure, containing conjugated double bonds, which results in enhanced chemical stability. In contrast, aliphatic organic compounds refer to those that form open chain molecular structures, instead of aromatic rings. Aromatic DOM is generally more recalcitrant than aliphatic DOM. Microbially derived DOM generally has a much lower aromaticity than terrestrially derived humic DOM, and absorbs less visible and UV light (McKnight et al.,
Moreover, aromaticity typically decreases with age and peat or soil depth as a result of longer residence times and greater microbial processing (O'Donnell et al., 2010; Cory and Kaplan, 2012; Inamdar et al., 2012), and consequently DOM becomes more labile.

Humification refers to the process of peat decomposition, which results in the production or accumulation of humic substances. It serves as an indicator of the age and bioavailability of OM, and is related to an increase in its recalcitrant and aromatic character (Chen et al., 2011).

Finally, hydrophobicity is a character of DOM that is based on the polarity of organic molecules. Humic substances generally belong to the hydrophobic (non-polar) fraction of DOM that is preferentially adsorbed to soils and is enriched in aromatic components, as opposed to protein-like substances that are relatively hydrophilic (polar) and bioavailable (Wershaw, 1999; Findlay and Sinsabaugh, 2003). Dilling and Kaiser (2002) reported that nearly all aromatic compounds occur exclusively in the hydrophobic fraction of DOM. Several studies have linked aromaticity with the hydrophobic fraction of DOM (Dittman et al., 2009; Dittman et al., 2010; O'Donnell et al., 2010).

The organic compounds that make up DOM are roughly 50% carbon by mass, and because of this, DOC is generally used to measure DOM in natural waters (Mitsch and Gosselink, 2007; Cory et al., 2011). Direct and indirect impacts of DOM on a variety of biological, chemical, and physical processes in water are well established (Mostofa et al., 2013). The quality (composition) and quantity of DOM alter light penetration in the water column (e.g., Markager and Vincent, 2000), are implicated in the complexation and transport of trace metals (e.g., Reuter and Perdue, 1977; Ravichandran, 2004) and pollutants (e.g., Her et al., 2003), influence nutrient dynamics, energy flux, and microbial communities (e.g., Wetzel, 1995), and perhaps most importantly, affect the global carbon cycle (e.g., Kayranli et al., 2010; Zepp et al., 2011).
1.2.2 Sources and Dynamics of DOM in High-Latitude Riverine Systems

Riverine DOM comes from a combination of sources, with groundwater, soil pore water, surface runoff, and tributaries all contributing to this DOM pool. Accordingly, the quality of riverine DOM is a reflection of the dynamic interactions of biogeochemical processes and hydrology of those sources and is thus subject to fundamental spatial and temporal variations (Jaffé et al., 2008).

In peatland systems, the composition and depth of the acrotelm and catotelm are deciding factors in the quality, concentration, and flux of DOM released to surface waters. Near-surface peat is a source of relatively ‘fresh’ or young allochthonous DOM derived from recently produced and actively decomposing vascular plant material, characterized by higher concentrations of lignin degradation products (Thurman, 1985; Amon et al., 2012). *Sphagnum* mosses for instance, have a high lignin content. Lignin degradation products, such as aromatic acids and phenols, increase the aromaticity and complexity of DOM, but have also been shown to control an increased production of DOM (Kalbitz et al., 2006). With increasing depth in the peat profile, DOM generally becomes more humified, but more microbially processed, reflecting older DOM with longer biological processing and residence times (100’s to 1000’s of years) (Thurman, 1985; D’Andrilli et al., 2010). However, decreases in humification with depth have been observed in bog and fen peatland sites, which suggests that, in some cases, the production of microbial protein-like DOM may exceed the microbial degradation of plant-derived humic DOM (Tfaily et al., 2015).

Peatlands may form over mineral soils that are low permeability and low conductivity layers, which limits flow and mass transport (Reeve et al., 2000). Aquifer materials (e.g., bedrock) typically contain near-negligible amounts of organic substances, and so little, if any, additional DOM is contributed to groundwaters (Thurman, 1985). However, where they exist, pipe networks, and karst bedrock features that contain relic OM and have higher hydraulic conductivities, may allow for the fast delivery of labile DOM groundwaters to surface waters.

In fluvial systems, DOM is prone to temporal variations in concentration and chemical composition that are primarily related to changes in discharge, frequency, and magnitude of storm events, and antecedent moisture conditions of landscape units that contribute to runoff.
(Hope et al., 1994; Jaffé et al., 2008; Saraceno et al., 2009; Miller and McKnight, 2010; Singh et al., 2013). Seasonality is especially pronounced in high-latitude rivers where air temperature, precipitation patterns, and snow cover change considerably throughout the year (Neff et al., 2006; O'Donnell et al., 2010; Mann et al., 2012; Walker et al., 2013). Peak flows that take place during spring freshet, generally in May or June of each year, have generated different DOM export responses in various northern catchments. During this time, runoff is routed overland and through near-surface peat, and contributes to a large flush of DOM to fluvial networks and other surface waters. It has been suggested that between 35 and 70% of annual DOC export in northern peatland surface waters occurs during freshet (Striegl et al., 2007; Dyson et al., 2011). In other northern peatlands, low river DOC concentrations immediately followed freshet and were noted to gradually increase with time as conditions dried out, leading to high DOC levels in the late summer (Moore, 2013; Orlova and Branfireun, 2014). More than half of the DOM discharged during freshet consists of young (1-5 years old), bioavailable fulvic acids, present in a proportionately higher concentration as compared to base flow (Hood et al., 2003; Neff et al., 2006; Raymond et al., 2007). During the typically dry summer months, a broad decrease in hydrological connectivity of surface water networks is commonly observed and, seepage from a deeper active layer and from the catotelm, contributes older and more humified DOM to surface waters. Correspondingly, summer discharge is characterized by lignin-poor DOM (Neff et al., 2006; Holmes et al., 2008). The prolonged base flow and warm temperatures in the summer can also promote optimal conditions for in-stream primary productivity and microbial metabolism (Thurman, 1985; Neff et al., 2006; Holmes et al., 2008), and thus increase the input of autochthonous, labile DOM (McKnight et al., 1994; Hood et al., 2003; Vazquez et al., 2010). The greater light availability in the summer can also lead to selective photodegradation of aromatic allochthonous DOM (Moran and Covert, 2003; Mann et al., 2012). In subarctic peatlands, enhanced precipitation in the late summer or autumn can result in a flushing of labile DOM that has accumulated in the peatlands during the dry summer and can constitute an ecological “hot moment”, a brief period of time that exhibits disproportionately high reaction rates relative to longer intervening time periods (McClain et al., 2003; Vidon et al., 2010; Singh et al., 2013; Ulanowski and Branfireun, 2013). With continued precipitation through the autumn however, DOM becomes diluted, while colder conditions slow the production of fresh OM (McClain et al., 2003; Moore, 2013). In the winter, discharge falls to an annual
low in the north, as rivers and streams partially or completely freeze-over, and any hydrological inputs that do contribute are limited to deep groundwater sources with typically low concentrations of less aromatic DOM (Striegl et al., 2007; O'Donnell et al., 2010).

On a shorter-term basis (hours to days), notable fluctuations in exports and quality of DOM occur during periods of high discharge, such as summer and autumn storm events (Hinton et al., 1997; Spencer et al., 2007; Inamdar et al., 2011). The quantity and quality of DOM flushed from pore waters by a storm depends a great deal on antecedent conditions, specifically the position of the water table relative to the peat surface. Extended dry summer periods, warm temperatures, and consequent lower water table position can encourage the breakdown and accumulation of allochthonous humic-like DOM (Fenner and Freeman, 2011). Hence, rainstorms preceded by drought-like conditions deliver rapid increases in DOM concentrations as the accumulated DOM is flushed from the surficial organic soils (Carey, 2003; Limpens et al., 2008; Inamdar et al., 2012; Singh et al., 2013). In contrast, consecutive rainfall events dilute the supply of DOM and reduce concentrations, causing a dampened DOM response (Carey, 2003).

1.2.3 Measures of DOM Quantity and Quality

The optical properties of DOM can be linked back to overall biogeochemical characteristics, and thus be used as a tracer of its function and variability in an ecosystem. The optically active fraction of DOM, referred to as chromophoric DOM (CDOM), absorbs light from visible to UV wavelengths (800 to 200 nm, respectively) (McKnight et al., 2001). However, a portion of CDOM also re-emits the absorbed energy as fluorescence; these molecules are called fluorophores, and constitute fluorescent DOM (FDOM) (Mopper et al., 1996). When a molecule absorbs energy, a loosely held electron is promoted to an excited energy level, where it loses some of its energy through vibrational relaxation and internal conversions. As the electron returns to its ground state, it emits residual excess energy as fluorescence. In effect, the re-emitted energy (emission) is always lower and has a longer wavelength than the initially absorbed energy (excitation); a phenomenon called the Stokes Shift (see Lakowicz, 2006; Reynolds, 2014). The excitation and emission wavelengths at which fluorophores fluoresce depend on their specific molecular structures. To aid in identifying individual fluorescence compounds, fluorophores are frequently categorized as humic-like, fulvic-like, or protein-like, according to how closely their fluorescent properties resemble those of humic
substances and proteins, respectively (Coble et al., 1993; Hudson et al., 2007). Such characterizations are essential in understanding the biogeochemical role of the DOM and the processes that produced it in various aquatic environments.

After its successful and continued application in marine environments (e.g., Coble et al., 1990; Parlanti et al., 2000; Guéguen et al., 2011), spectroscopic characterization of DOM has become an increasingly prevalent approach for the evaluation of DOM quality and quantity in numerous freshwater systems (e.g., Mladenov et al., 2007; D’Andrilli et al., 2010; Inamdar et al., 2011; Amon et al., 2012). The many indices measured through UV and fluorescence spectroscopy provide precise and detailed information about DOM quality that is unattainable through conventional, quantitative measurement of DOC concentrations. Spectroscopic techniques offer a method of elucidating a broad range of temporal and spatial trends in DOM source and concentration, such as variations in aromaticity, redox state, bioavailability, and composition (terrestrial and aquatic sources) (Jaffé et al., 2008; Miller and McKnight, 2010; O’Donnell et al., 2010; Mann et al., 2012). Moreover, UV and fluorescence spectroscopy deliver a rapid and straightforward approach to DOM characterization, at a fraction of the cost of conventional analytical techniques (e.g., chromatography). Advances in this technology over the past 10 years have led to improved multivariate analysis techniques (Cory and McKnight, 2005; Murphy et al., 2013), and the more recent application of in situ instrumentation in water quality monitoring studies to attain high-resolution, time-resolved information on DOM dynamics (Saraceno et al., 2009).

A prevalent indicator in the characterization of DOM quality is the specific ultra-violet absorbance (SUVA) (Weishaar et al., 2003). Specific UV absorbance is calculated as the absorbance of a sample at 254 nm (m\(^{-1}\)) divided by its DOC concentration (mg C L\(^{-1}\)) (Weishaar et al., 2003; USEPA, 2009). The measure of SUVA is strongly and positively correlated with DOM aromatic carbon content (Weishaar et al., 2003), and is thus a satisfactory indicator of DOM aromaticity, which varies with chemical composition and source (e.g., Saraceno et al., 2009).

The fluorescence index (FI) has become a widely used measure of DOM quality, and is calculated as the ratio of fluorescence intensities of emission wavelengths 470 nm and 520 nm, obtained at an excitation wavelength of 370 nm (Cory and McKnight, 2005). The FI is
an indicator of DOM source, where high FI values (~1.8) indicate autochthonous DOM, and low values (~1.2) are consistent with allochthonous sources (McKnight et al., 2001; Cory and McKnight, 2005). Intermediate values of FI indicate that some mixing has occurred, while a difference in FI values of 0.1 or more between samples may be suggestive of a change in DOM source (McKnight et al., 2001). In addition, FI has been found to have significant and negative correlations with SUVA (Jaffé et al., 2008) and DOC concentrations (Wu et al., 2007).

Humification index (HIX) functions as a diagnostic index of DOM quality, in addition to SUVA, FI, and numerous others. Humification index was first calculated by Zsolnay et al. (1999) by dividing the area in the 435-480 nm region of the emission spectra by that of the 300-345 nm region, obtained at excitation 254 nm. Variations of this calculation are also commonly used (Kalbitz et al., 2000; Ohno, 2002) to determine the degree of natural OM humification. For instance, Ohno (2002) modified the HIX denominator to the combined areas of the 300-345 nm and 435-480 nm regions of the emission spectra, making HIX more robust to variance caused by DOM concentration and inner-filter effects (IFEs). The HIX value ranges from 0 to 1, with higher values indicating an increasing degree of humification (Ohno, 2002).

Finally, FDOM sensors have frequently been used to quantify humic substances in aquatic systems, typically using fluorescence around excitation 370 nm and emission 460 nm (Pellerin and Bergamaschi, 2014), however the broad excitation and emission peaks used for standard FDOM measurements differ by sensor manufacturer. Measurement of FDOM has also been used for its ability to predict DOC concentrations in range of ecosystems (e.g., Downing et al., 2009; Saraceno et al., 2009), but since only a portion of DOM fluoresces, and this fluorescence depends on DOM composition, the strength of the relationship between FDOM and DOC varies between environments, watersheds, and flow conditions.

In order to acquire a wider range of information about the composition of DOM within a water sample, a more detailed measurement of DOM fluorescence known as an excitation-emission matrix (EEM) is used. Excitation-emission matrices are produced through the concatenation of successive emission spectra at a range of excitations into a three-dimensional plot of fluorescence intensities (Coble, 2007). Excitation-emission matrix
spectroscopy has rapidly developed into a prevailing method of DOM characterization (Coble et al., 1990; Coble, 1996; McKnight et al., 2001; Inamdar et al., 2011). Analysis of EEMs allows for differentiation of fluorophore classes of allochthonous and autochthonous DOM, which is facilitated through the use of parallel factor (PARAFAC) analysis, a multivariate modeling technique. PARAFAC provides a breakdown of the DOM fluorescence signature into unique groups of fluorophores, or components, as well as an estimate of their relative abundances based on the position and intensity of peaks identified in the EEM. Moreover, PARAFAC modeling returns various diagnostic indices; combined with the identified component, these indices yield valuable information related to the source, mixing, bioavailability, photodegradation, and humification of DOM within a sample. Several reviews and tutorials are available for EEMs and PARAFAC, and offer elaboration on the abovementioned topics (Bro, 1997; Stedmon and Bro, 2008; Fellman et al., 2010; Murphy et al., 2013).

1.2.4 The Mercury-DOM Relationship

Mercury (Hg) is a global environmental pollutant, and is of particular concern in peatlands, as the methylated organic form, methylmercury (MeHg), bioaccumulates in the food chain, and is a potent neurotoxin, thus posing detrimental health risks to humans, fish, and other wildlife. Mercury is derived from both natural and anthropogenic sources. Emission from anthropogenic sources, mainly industrial activities and artisanal and small-scale gold mining, are responsible for the majority of the current atmospheric Hg burden (UNEP, 2013), which has increased by a factor of two to three in the past 200 years (Mason et al., 1994; Driscoll et al., 2007). Typically, Hg enters the atmosphere as gaseous elemental Hg (Hg\(^0\)), which has a relatively long atmospheric residence time (ca. 9 months) (Lindberg et al., 2007). Through various atmospheric processes, Hg\(^0\) is oxidized to various water-soluble forms (Hg(II) compounds). Atmospheric dispersal of Hg\(^0\) enables its far-reaching dry and wet deposition as Hg(II) species, causing it to be the dominant source of Hg in remote aquatic ecosystems (Fitzgerald et al., 1998). Once deposited, various abiotic and biotic reactions, including methylation, transform Hg (Morel et al., 1998). At northern latitudes especially, peatlands are central to the production, transport, and biogeochemical fate of Hg, particularly MeHg (St. Louis et al., 1994; Branfireun et al., 1999; Branfireun and Roulet, 2002; Branfireun et
al., 2005), due to their inherent organic soil properties, hydrology, residence times, reducing conditions, and microbial and chemical processes.

Dissolved organic matter has a strong and well-documented relationship with Hg in aquatic environments, specifically total mercury (THg) and MeHg (Mierle and Ingram, 1991; Ravichandran, 2004; Brigham et al., 2009). The complexation between Hg and DOM facilitates the transport and solubility of Hg, affects its toxicity, and has been known to affect its bioavailability to methylating bacteria (Driscoll et al., 1995; Ravichandran, 2004). The overwhelming quantity of DOM held in peatlands includes trace amounts of sulfur-containing functional groups that bind Hg preferentially over other functional groups (Ravichandran, 2004). Likewise, the findings of Hill et al. (2009) suggest that MeHg has a higher affinity for low molecular weight aromatic DOM fractions, of which wetlands appear to contain a greater percentage due to increased microbial processing, relative to rivers and lakes. Furthermore, since allochthonous and autochthonous sources of DOM may differ in molecular size, the origin of DOM plays an essential role in the spatial and temporal variability of MeHg-DOM binding and MeHg contributions to surface waters (Hill et al., 2009). In wetlands, where anaerobic conditions prevail, sulfate-reducing bacteria are the principal methylators mediating the transformation of inorganic Hg into MeHg (Compeau and Bartha, 1985; Ullrich et al., 2001). Befitting of the abundant supply of DOM, long residence times, and ideal conditions for sulfate reduction, peatlands are regarded as having enhanced potential for Hg methylation and MeHg mobilization, as compared to upland ecosystems (Branfireun and Roulet, 2002; Brigham et al., 2009). Changes in the quality and quantity of DOM occur as a result of short-term and gradual long-term hydrological variation, and influence Hg dynamics and fluxes in aquatic ecosystems (Dittman et al., 2010). Because of this relationship, fine temporal scale monitoring is beneficial to studies of both DOM and Hg.
1.3 Water Quality Monitoring and DOM Optical Properties as a Proxy Technique

Currently, conventional water quality monitoring programs employed in remote northern environments involve the collection of water samples at relatively infrequent intervals (weeks to months). However, due to the episodic nature of storm events, such campaign-based sampling programs often fail to capture the solute fluxes of DOC and Hg associated with these high-flow periods (Hinton et al., 1997; Dittman et al., 2009). Because DOC export is typically highest during storm events and varies with antecedent conditions, a lack of sampling during high flows can lead to significant underestimates of stream or river DOC fluxes (Hinton et al., 1997). Although some statistical estimation techniques (e.g., adjusted maximum likelihood estimation) exhibit negligible bias in estimating solute loads, when measurements are not normally distributed, as is the case for episodic storm events, these methods become less reliable, especially over lengthy time intervals (Cohn, 2005). The time and cost of an increased sampling frequency to capture streamflow dynamics limit its applicability and constitute a need for an alternative high-resolution sampling strategy.

Advances in spectroscopy have shaped it into a more flexible, rapid, and affordable technology that has become an attractive and simple diagnostic tool for water quality monitoring (Hudson et al., 2007). Discrete and in situ measurements of optical properties, including FDOM, FI, and SUVA, have been used to indicate seasonal and event-based shifts in DOM source, quantity, and quality (Saraceno et al., 2009), and have been useful proxies for THg (Dittman et al., 2009) and MeHg (Bergamaschi et al., 2011) dynamics. However, although many studies have found strong correlations between DOM, THg, and MeHg and optical measurements, correlation strengths are not always consistent, and vary depending on the DOM composition in different ecosystems (Coble, 2007). In effect, an optical measurement serving as a useful proxy in one environment may not be applicable as an equally useful proxy in another.

In situ spectroscopic measurements have developed into a more frequently applied tool in water quality monitoring of marine, estuarial, and more recently freshwater environments. This technique allows for the nearly continuous measurements needed to resolve short-term or episodic solute fluxes (on the order of seconds to hours), which may be difficult to attain with conventional sampling methods. In situ monitoring of FDOM has proven to be highly
effective in disambiguating the spatiotemporal variability of DOM (Spencer et al., 2007; Bergamaschi et al., 2011; Downing et al., 2012; Pellerin et al., 2012). The measurement of FDOM excitation and emission wavelengths (ex 325 nm, em 470 nm) acts as an indicator of humic substances, the largest fraction of DOM in natural waters. The humic fraction of DOM is also closely tied with Hg (Mierle and Ingram, 1991), and is the reason for FDOM measurements succeeding as a proxy for THg and MeHg (Bergamaschi et al., 2012), although this strategy has not been extensively applied. Meanwhile, in the northeastern United States, Dittman et al. (2010) did not observe a correlation between MeHg and DOM with a traditional sampling approach, indicating that FDOM measurements would be an ineffective predictor of MeHg concentrations. This suggests that the success of utilizing FDOM measurements as a proxy for Hg concentrations is not universal and is likely to vary between different aquatic environments.

1.4 Thesis Objectives and Structure

The Hudson Bay Lowlands (HBL) is the second largest contiguous peatland in the world (320,000 km²), covering over half of Ontario’s Far North (Roulet et al., 1994; FNSAP, 2010), and to a lesser extent, parts of Manitoba and Quebec. Peatlands contain about 56% of Canada’s total terrestrial soil carbon (Tarnocai, 2006); roughly one quarter of this (35 Gt of carbon) is estimated to be stored in the HBL in an extensive cover of peat, up to 3 meters deep (Roulet et al., 1994; FNSAP, 2010). However, the storage of carbon will likely be disrupted, as the high northern latitudes at which the HBL resides are projected to be among the most affected by global climate change (IPCC, 2007), and could trigger large positive feedbacks to the climate system through peatland emissions of greenhouse gases (Limpens et al., 2008). The network of rivers and tributaries that flow through and connect the peatlands of the HBL exports peatland-derived water and solutes (e.g., DOM and associated atmospherically deposited Hg) to downstream aquatic ecosystems, such as Hudson and James Bay. Mercury is of particular concern to downstream communities of the HBL (especially the Mushkegowuk Council First Nations), since MeHg bioaccumulates in fish and poses a severe health risk to those who consume fish regularly. High Hg concentrations have been observed in northern subsistence fish populations for some time, and have led to consumption advisories in the HBL region (MOECC, 2013). In addition, recent land use
changes and resource extraction projects, such as the De Beers Victor Diamond Mine, have heightened existing concerns regarding Hg loading into rivers that drain the HBL.

Water quality monitoring programs can help elucidate spatiotemporal changes to aquatic environments in the HBL, including increases in DOC concentrations in water, Hg concentrations in fish, and the biogeochemical processes that contribute to them. However, the remoteness and vastness of the HBL restrict widespread, high-resolution monitoring from taking place due to logistical constraints and the high costs associated with implementing traditional campaign based sampling projects. Meanwhile, advances in optical sensor technology for resolving DOM quality and Hg concentrations in situ have led to an increasingly common application of this technique in water quality monitoring programs of natural waters over the past two decades. While originally utilized in strictly marine applications, portable DOM optical sensors are now being used in freshwater systems, allowing for real-time monitoring of DOM variability in environments where high-resolution data would be otherwise difficult to collect. Multi-channel loggers equipped with optical sensors are also relatively cheap, representing a one-time cost for instrumentation and minimal costs associated with infrequent travel to sampling sites for installation and maintenance purposes only. In comparison, physical sampling campaigns accumulate costs for more frequent travel, as well as for sampling and analysis. In addition, advances in logger technology have made it possible to access the high-resolution optical data collected remotely via telemetry for an increasing number of logger designs, thus decreasing the need for travel to data collection sites. Despite the potential benefits of such a monitoring approach, in situ absorbance or fluorescence monitoring has not been applied in waters of a vast peatland complex, such as the HBL.

Some of Canada’s largest rivers, such as the Attawapiskat, Moose, and Albany drain into the Hudson Bay (Riley, 2011). These large rivers provide substantial inputs of runoff and terrestrial DOM to Hudson Bay, that consequently influence biomass, thermodynamics, and stratification of its waters (Granskog et al., 2007), presenting a need for a comprehensive monitoring strategy. The abundance of CDOM in the Hudson Bay and Hudson Strait system (Granskog et al., 2007) suggests that absorbance and fluorescence measurements would be a useful tool for DOM analysis in the HBL watershed. While the remoteness of the HBL makes traditional sampling impractical, the high CDOM content of its rivers coupled with the
durability, flexibility, and economical benefits of optical measurements, make this a promising approach for *in situ* riverine monitoring in this system. Despite its breadth, its importance in the global carbon cycle, and growing concerns over its mercury content, our understanding of how peatlands of the HBL behave hydrologically and how they may respond to external forcings, such as climate and land use change, is scant (Keller *et al.*, 2014).

In Chapter 2, I aim to evaluate spatial and temporal changes in riverine DOM spectroscopic properties as a reflection of contributing source waters throughout the ice-free period (spring to autumn) in rivers of the HBL. I also aim to determine if other sources of DOM, such as in-stream production and microbial processing factor into the chemistry of these rivers, which are typically assumed to be low-productivity and nutrient-poor surface waters. Findings will contribute to our current understanding of the hydrological behaviour and functioning of peatlands in the HBL. Samples collected from two rivers in the HBL (the North Granny Creek and the Nayshkootayaow River) and from a variety of potential peatland DOM sources (*e.g.*, bogs, fens, and deep groundwater) are used to characterize DOM through concentration and quality (optical measurements), and ancillary chemistry (stable isotopes of water and major ions) for different stages of hydrological connectivity, and ultimately interpret changes in the principal sources of DOM to surface waters throughout the study period, including important in-stream processes.

In Chapter 3, I assess the viability of optical measurements for widespread use as *in situ* proxies for DOC, THg, and MeHg in the HBL. In addition, I aim to establish factors that may confound the effectiveness of these optical measurements as proxy measurements, including changes in the quantity and quality of DOM, and sensor performance. I evaluate analytical solute measurements and *in situ* and laboratory-based fluorescence and absorbance measurements, specifically FDOM, SUVA, and FI, over the course of the study period in the two rivers from Chapter 2, which are different sizes and stream orders: the North Granny Creek being a second order stream, and the Nayshkootayaow River, a fourth order stream. Using correlations between solutes and optical measurements, I build on the spatial and temporal variability observed in Chapter 2 and investigate restrictions of these optical measurements caused by in-stream primary production and microbial processes, and high DOC concentrations.
1.5 References


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CHAPTER 2

2 Peat, primary production, and secondary processing characterize dissolved organic matter in rivers of the Hudson Bay Lowlands, Ontario

2.1 Introduction

Northern peatlands contain approximately 25% of the world’s terrestrial carbon (Roulet et al., 2007), accumulated over ca. 10,000 years. The Hudson Bay Lowlands (HBL) is the second most extensive peatland complex in the world and constitutes a large fraction of this carbon store with ca. 35 Gt of carbon in a peat layer (0 to 3 m thick) over 320,000 km$^2$ (Roulet et al., 1994; FNSAP, 2010). The peatlands that cover the majority of the HBL consist primarily of bog and fen peatland types, although others, such as swamps, and permafrost peat mounds and plateaus (palsas) are also present (Riley, 2011). This low-gradient peatland dominated landscape is characterized by a complex drainage network that delivers freshwater and solutes to the James and Hudson Bays and ultimately the Arctic Ocean (Rouse et al., 1992). However, data with respect to hydrology in the region is principally focused on large rivers (e.g., Déry et al., 2005; Déry et al., 2011), and thus our understanding of the nature of the hydrological interactions between peatland-dominated watersheds and the smaller channels that drain them is largely conceptual. Also, with the exception of a few key studies (e.g., Granskog et al., 2007; Kirk and St. Louis, 2009), scientific knowledge about the chemistry of freshwaters in the HBL is scarce. Being peatland-dominated, one of the more abundant solutes evolving from these watersheds is dissolved organic matter (DOM).

The concentration (quantity) and composition (quality) of DOM in fluvial systems are of significant interest because of their importance for aquatic ecosystem metabolism (e.g., Wetzel, 1984), role in the carbon balance of watersheds (e.g., Schlesinger and Melack, 1981; Limpens et al., 2008), and strong relationship to the transport and bioavailability of pollutants such as mercury (e.g., Ravichandran, 2004; Aiken et al., 2011). Dissolved organic matter quantity and quality are seasonally variable, and are highly influenced by catchment hydrology, land cover, temperature, and the sources of organic matter, which broadly may be allochthonous (terrestrial; largely derived from decomposition of more complex biological materials), autochthonous (aquatic; largely derived from microbial processes and primary
production, *e.g.*, algae, bacteria), or some combination of the two (see Findlay and Sinsabaugh, 2003). The molecular composition of DOM results in variations in its biological availability or reactivity, and is therefore commonly referred to as either “labile” (more so) or “recalcitrant” (less so). Labile DOM generally constitutes a smaller proportion (10–40%) of DOM and is readily available for microbial decomposition, while the remaining proportion of DOM is considered recalcitrant and is mostly resistant to rapid biodegradation (Søodergaard and Middelboe, 1995; Tranvik and Kokalj, 1998). Generally, allochthonous DOM is considered to be more recalcitrant than autochthonous DOM (Søodergaard and Middelboe, 1995). However, recent studies suggest that allochthonous DOM fuels a smaller but steady amount of microbial metabolism (Guillemette and del Giorgio, 2011), and since bacteria preferentially utilize the more labile fraction of DOM first, recalcitrant allochthonous DOM may become a relatively more important source in the pool of available DOM on longer timescales (*i.e.*, months to years), when isolated from fresh inputs (Koehler *et al.*, 2012). The bioavailability of DOM is influenced by many intrinsic (*e.g.*, source, aromaticity) and extrinsic (*e.g.*, temperature, oxygen availability, light) factors (see Del Giorgio and Davis, 2003). For instance, humic aromatic organic molecules are highly susceptible to photodegradation, which results in a breakdown of their aromatic structure into a more bioavailable form (Moran and Covert, 2003). Aromaticity describes carbon compounds that have a molecular ring structure with conjugated double bonds, which results in those compounds gaining enhanced stability and thus recalcitrance, as opposed to aliphatic compounds, characterized by an open chain molecular structure. Terrestrially derived humic DOM is generally more aromatic than microbially derived DOM (McKnight *et al.*, 1994). Meanwhile, humification, which results from various biotic and abiotic processes of peat decomposition, provides an indication of the age and bioavailability of DOM, where increased humification is associated with greater recalcitrance and aromaticity (Chen *et al.*, 2011).

In extensive peatlands like the HBL, contributions of water and solutes to surface waters may be from shallow groundwater and pore waters in the peatlands themselves, as well as from deeper groundwaters discharging from underlying sediment and bedrock aquifers (Orlova and Branfireun, 2014), with the quantity and quality of water derived from each compartment being quite distinct. Likewise, different peatland types, and their hydrological compartments,
have different DOM characteristics. For instance, Fraser et al. (2001) found that peatland DOM becomes more autochthonous-like, and less aromatic with depth. However, contrasting findings regarding depth-related DOM characteristics have been reported. In bogs, relatively high levels of aromatic DOM were found to be present throughout the peat profile due to its lignin-rich source (sphagnum mosses), and generally became more recalcitrant at depth (D’Andrilli et al., 2010). In fens, a greater abundance of highly productive vascular plant types and enhanced nutrient cycling and decomposition were suggested to contribute to a greater proportion of labile DOM at the surface of the peat profile, and therefore relatively less aromatic DOM than in bogs (Fellman et al., 2008; D’Andrilli et al., 2010; Tfaily et al., 2013). Deep groundwaters, such as those from bedrock aquifers, typically have lower DOM concentrations and are characterized by older, labile and less aromatic DOM than peat sources, as a result of more microbial processing and longer residence times (O'Donnell et al., 2010; Inamdar et al., 2012). Because DOM source waters typically change with season, so do the characteristics of organic matter entering surface waters (e.g., Neff et al., 2006; O'Donnell et al., 2010; Singh et al., 2013). Knowing the quality of DOM from different end-members or sources and their relative contributions to peatland surface waters may help us to better comprehend peatland catchment hydrologic connectivity, which relates to the degree to which the connection of landscape components with a drainage network facilitates the flow of water and solutes within the peatland, as well as the seasonal changes in surface water DOM quality that follow.

The optically active portion of DOM, called chromophoric DOM (CDOM), provides a method of characterizing how various aspects of the quality of DOM, as well as its amount in stream water, change seasonally. For instance, spectroscopic analysis of specific UV absorption (SUVA) of CDOM as a whole, and of the fluorescence properties of its fluorescing fraction (FDOM) offer information on temporal and spatial trends in DOM source and concentration, such as variations in age, reactivity, and relative composition (autochthonous vs. allochthonous) (Moore, 2013). Previous studies have demonstrated that DOM derived from different sources and different flow paths can have unique composition and spectroscopic properties (Neff et al., 2006; Raymond et al., 2007; Holmes et al., 2008; Spencer et al., 2009; Stedmon et al., 2011). Much of this research has focused on major watersheds contributing to the Arctic basin, however these spectroscopic methods have rarely
been employed within subarctic peatland complexes, including the HBL (Granskog et al., 2007), and have yet to be employed in situ in these ecosystems. Here, they could help elucidate the complicated and relatively understudied relationship of hydrology and seasonal changes in peatland connectivity.

In remote regions like the HBL, studies of hydrological connectivity and landscape contributions to riverine chemistry can be difficult and expensive to undertake, and thus are typically limited in their spatial and temporal scale. In effect, traditional campaign-based water quality monitoring strategies are generally restricted by relatively few grab samples collected in summer months, require substantial interpolation of results, and are not well suited for determining inputs to the complex fluvial systems of these remote peatland areas due to their limited spatial and temporal scales. Therefore, the ability of spectroscopic methods to characterize and “fingerprint” various potential contributing watershed sources at high temporal resolutions throughout more of the year may help us to understand which sources contribute and when to river waters, and elucidate the hydrology of the HBL peatland landscape.

Currently, the interaction of rivers and their surrounding landscape in the HBL is largely understudied, and is poorly understood. The purpose of this study was therefore to determine what sources of water and chemistry are the most influential contributors to rivers of different size, structure, and stream order in the HBL, and to determine how source water contributions change throughout the ice-free season. Within this goal, this study aimed to establish if any unidentified sources or in-stream processes influence river chemistry, besides the expected peatland and groundwater inputs. Water from two river within a shared watershed of the HBL, as well as of various potential contributing sources (bog, fen water track, and fen shallow and deep pore waters, and deep clay and bedrock groundwater) are also characterized through spectroscopic and ancillary chemical analyses to provide descriptive characterizations that will assist in identifying how the quality of water and DOM changes at different seasonal stages of hydrological connectivity. Spatial and temporal changes in these characteristics are evaluated and compared for the surface waters of the two rivers throughout the ice-free season. Spectroscopic measurements provide useful information of DOM aromaticity, with SUVA (Weishaar et al., 2003), relative composition (allochthonous vs. autochthonous), with fluorescence index (FI) (McKnight et al., 2001;
Cory and McKnight, 2005), and degree of humification, using the humification index (HIX) (Ohno, 2002). These techniques enable us to distinguish which sources are contributing, and therefore provide information on the potential flow path and processing of DOM over the course of the study period. We propose that the characterization of DOM, along with ancillary chemistry, will provide a useful tool for elucidating hydrological inputs and connectivity, and therefore improve our current understanding of the complex hydrology of the HBL’s peatland landscape.

2.2 Study Site

Samples were collected from the North Granny Creek sub-catchment (30 km$^2$), and the larger Nayshkootayaow River catchment (1,721.8 km$^2$), which drain into the Attawapiskat River approximately 90 km west of Attawapiskat, Ontario (52.82°N, 83.88°W) (Figure 2.1). The Attawapiskat River (total catchment area = ca. 50,500 km$^2$) supplies substantial amounts of freshwater and associated solutes, including organic matter, to the downstream Hudson/James Bay. The study area is part of the James Bay Lowland (JBL), within the Hudson Bay Lowlands ecozone, which primarily consists of a remote and pristine assemblage of peatland types.

The climate of the study area is generally cold continental with moderate precipitation, averaging 700 mm per year. Approximately 70% of this falls as rain, mostly during the summer growing season between June and September for the Lansdowne House meteorological station, located approximately 280 km west-southwest of the study site (Environment Canada, 2014). Geologically, the Hudson Platform, which consists of ca. 250 m thick Paleozoic limestone, mudstone, dolostone, and evaporite, underlies the study area (Singer and Cheng, 2002). Over the course of the Quaternary period, the sequence of the Laurentide Ice Sheet followed by deglaciation and the emergence of the shallow Tyrell Sea (ca. 8,000 years ago) resulted in an overburden of glacial tills, marine silts and clays, of low hydraulic conductivity ($1 \times 10^{-6}$ to $1 \times 10^{-8}$ m s$^{-1}$) (Whittington and Price, 2012), which accumulated to thicknesses of between 10 and 30 m (Glaser et al., 2004). Together with the poor drainage of the area, the continued isostatic rebound of the Hudson Bay region (10 mm y$^{-1}$) over the past ca. 6,000 years and consequential flattening of the regional landscape slope,
have encouraged the gradual accretion of peat deposits up to 3 m in thickness, and development of an extensive peatland-dominated landscape within the HBL (Riley, 2011).

Figure 2.1: Maps showing (a) the location of the study area in the Hudson Bay Lowlands (HBL; dark grey) within Ontario (light grey), and (b) the locations of the North Granny Creek (NGC) and Nayshkootayaow River (NR) sampling sites (black circles) and their respective drainage areas, peat pore water sampling transects, namely the Bog-Fen Transect (BFT) in the NGC sub-catchment and the Ministry of Environment and Climate Change (MOECC) research transect in an upstream sub-catchment of the NR (white stars), as well as the Victor Mine open pit (black diamond).

Vegetation types in the study watershed are typical of the Hudson Bay Lowlands ecozone, and depend on peatland type. Bogs are raised domed landforms relative to the surrounding peatland landscape. They are disconnected from groundwater sources, and are characterized in the region by a vegetation cover dominated by Sphagnum mosses, lichens (Cladonia spp.), and brown mosses (Amblystegiaceae spp.), with a sparse overstory of ericaceous shrubs, such
as leatherleaf (*Chamaedaphne calyculata*) and Labrador tea (*Rhododendron groenlandicum*), as well as black spruce (*Picea mariana*). Fen landforms, often distinguished by distinctive patterning of alternating ridges and pools, groundwater and surface water movement, minerotrophic characteristics, and near-surface water table, consist of a more diverse vegetation assemblage than bogs (NWWG, 1997). Of the most prominent fen species are sedges (*Carex* spp. and *Scirpus* spp.), sweet gale (*Myrica gale*), horsetails (*Equisetum fluviatile*), and stunted tamarack (*Larix laricina*) (Glaser *et al.*, 2004). In better-drained riparian areas of the Nayshkootayaow River watershed, denser treed or forested areas are populated by speckled alder (*Alnus rugosa*), white birch (*Betula papyrifera*), white and black spruce (*Picea glauca* and *mariana*), balsam fir (*Abies balsamea*), and balsam poplar (*Populus balsamifera*) (Singer and Cheng, 2002; Riley, 2011).

The presence of the De Beers Victor Diamond Mine in the vicinity means that surface waters and peatland groundwaters in both watersheds are affected to some degree by the cone of groundwater depression resulting from open-pit pumping and dewatering activities that extends several kilometers in diameter. Peatland pore water and shallow groundwater samples from bog, fen water track and fen features were obtained from two existing research transects (Whittington *et al.*, 2012; Whittington and Price, 2012; Ulanowski and Branfireun, 2014). The first sampling transect for peat pore water sampling is located in the North Granny Creek sub-catchment, which lies partially within the zone of mine impact, and is 1500 m long, transecting several fen and bog features. The other peatland sampling site is located at the Government of Ontario’s Ministry of Environment and Climate Change (MOECC) long-term carbon monitoring program study site (52.70°N, 83.60°W), approximately 15 km south of the Nayshkootayaow River sampling site, well outside of the mine-impacted zone (Ulanowski and Branfireun, 2014). The transect lies within an upstream sub-catchment of the Nayshkootayaow River and intersects approximately 600 m of a bog feature and another 600 m of the adjacent ribbed fen.

The Nayshkootayaow River is a fourth-order river (Strahler order) that flows into the Attawapiskat River, to the east of the mine. The North Granny Creek, a second-order tributary that forms at the confluence of two first-order peatland streams, flows into the Nayshkootayaow River, downstream of the Nayshkootayaow sampling site. The North Granny Creek channel is incised only into the peat layer, with marine sediments often
defining the streambed. Meanwhile, the Nayshkootayaow River is incised into bedrock due to larger-scale fluvial processes and base-level fall resulting from postglacial rebound. As such, bedrock is exposed along much of the river’s banks and streambed. Groundwater discharge from the bedrock aquifer system also feed base flow in the river and affect its chemistry (Orlova and Branfireun, 2014). To mitigate the effects of mine dewatering on stream flow and on the health of fish populations, water from the nearby Attawapiskat River is diverted via a water pipeline for flow supplementation of the Nayshkootayaow River during low flow periods. The supplementation output is located upstream from the Nayshkootayaow sampling site. Despite supplementation, the Nayshkootayaow River provides an easily accessible sampling site that is representative of river waters in channels of similar size in the region. For the study period, supplementation was initiated on July 6, and continued at a steady rate of ca. 12,000 m³ day⁻¹ until August 15, 2013, representing approximately 15-20% of total flow at the site during that time (D. Ott, De Beers Group of Companies, personal communication, 2014).

2.3 Methods

2.3.1 Hydrological Monitoring and Watershed Sampling

Streamflow discharge for the Nayshkootayaow River was measured as part of the mine operations and data was provided by the De Beers Group of Companies. Water level was recorded every 15 minutes using a submerged Schlumberger Micro-Diver transducer (accurate to ± 0.01 m). Stage measurements were converted to discharge using a stage-discharge rating curve generated between 2000 and 2013 (D. Ott, De Beers Group of Companies, personal communication, 2014). Monthly manual discharge measurements at the mine are also acquired using a SonTek® FlowTracker® Acoustic Doppler Velocimeter. Similarly, discharge for the North Granny Creek was calculated using pressure transducer measurements, corrected for barometric pressure, and a 15-point rating curve from the 2012 field season. Precipitation and air temperature data is available at 10-minute intervals from a De Beers weather station located approximately 2 km northwest of the mine, and less than 1 km from the North Granny Creek sampling site, providing weather data that was more locally representative than regional data from Lansdowne House.
Manual sampling of river waters took place during three study periods in 2013, occurring in spring (June 5 to June 22), summer (July 11 to August 15), and autumn (October 16 to 25), selected based on *a priori* knowledge of the general seasonality of the study region. Spring samples were collected during the freshet hydrograph recession. During sampling periods, grab samples were collected from the Nayshkootayaow River and the North Granny Creek every 1 to 2 days, alongside in-stream high-resolution logger measurements. In addition to the river water sample collection, samples were also collected from peatland pore waters and groundwaters during the spring and summer sampling periods. Samples used to characterize these sources were collected from surficial peatland pore waters (integrated 0-5 cm, relative to the water table), as well as from existing shallow (defined as 50 and 90 cm relative to the peat surface, r.t.s.) and deep (150 cm r.t.s.) piezometers in bogs, fen water tracks and fens along the North Granny Creek transect and the MOECC site. As part of a previous study, piezometers were constructed using 0.125 m I.D. Schedule 40 PVC pipe, and were slotted for a 0.1 m intake at the base. The slotted intake was also fitted with 250 μm Nitex® nylon mesh as a screening material to prevent piezometer clogging. Piezometers were installed in nested configurations, with a nest consisting of four piezometers installed at various depths below the peat surface (typically 0.5 to 2.0 m). Piezometer and surface pore water samples were acquired using a low-flow peristaltic pump and pre-cleaned, acid-washed, polytetrafluoroethylene (PTFE) tubing.

Surface pore water sampling was accomplished using an additional PTFE pore water sipper (0.0125 cm inner diameter; 5.0 cm slotted intake) inserted into the upper 5 cm of the water table in undisturbed areas of peat near sampled piezometer nests. Each surface sample was a composite of pore waters from three separate points within 1 meter of piezometer nests in order to account for the local variability in water chemistry in peatlands (Ulanowski and Branfireun, 2013). Piezometers were purged approximately 24 hours prior to sampling to remove standing water and ensure a fresh and representative sample, and sample tubing was rinsed through with DI water between samples to prevent cross-contamination. Between 125 and 250 mL of sample was pumped into new sterile polyethylene terephthalate glycol-modified (PETG) bottles, with field blanks and duplicates included for every ca. 10 samples. Deep groundwater samples were collected from De Beers Victor Mine monitoring stations and were provided courtesy of the mine’s Environment Department. Deep groundwater...
piezometers at these sites are installed into bedrock and deep clays, to depths of between 4 and 20 m beneath the ground surface.

2.3.2 Sample Processing and Analysis

All samples were vacuum filtered through acid-rinsed 0.45 μm regenerated cellulose filter papers (Whatman RC55) using a PTFE filtration apparatus within 24 hours of collection. A subsample for stable isotopes of water was poured into 20 mL high-density polyethylene (HDPE) scintillation vials, sealed with PTFE-lined displacement caps, and stored without headspace. Samples for cations, anions, DOC, and DOM absorbance and fluorescence analyses were stored in 60-100 mL amber glass bottles without headspace. Once filtered, samples were stored in the dark at 4°C until analysis. Samples were kept cold during shipments from the De Beers Victor Mine to analytical laboratories at the University of Western Ontario (Ecohydrology Lab and the Biotron Experimental Climate Change Research Centre; London, Ontario), and were refrigerated immediately and until analysis.

Samples were analyzed for DOC concentration using an OI Analytical Aurora 1030W TOC analyzer with heated sodium persulfate oxidation (Method Detection Limit, MDL = 0.1 mg L\textsuperscript{-1}). Cations (Na\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, K\textsuperscript{+}, Al\textsuperscript{3+}, Si, and others) and anions (Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}) were analyzed in the Biotron (CALA ISO 17025 certified) using Dionex ICS-3000 and Dionex ICS-1600 Ion Chromatography systems, respectively (some data not presented). Limits of detection for major ions were typically between 0.1-0.5 mg L\textsuperscript{-1}. Analysis of stable isotopes of water (δD and δ\textsuperscript{18}O) was performed on a Picarro L2120-i δD/δ\textsuperscript{18}O Isotopic Water Analyzer (VSMOW, precision: δD ± 0.5 ‰, δ\textsuperscript{18}O ± 0.1 ‰) that utilizes cavity ring-down spectroscopy (CRDS) to attain high-precision measurements. A Local Meteoric Water Line (LMWL) for stable isotopes of water was established based on samples of rain and snow collected within a 15 km radius of Victor Mine from 2008-2013. Quality control (QC) procedures for DOC, ion, and isotope analyses were maintained through blanks (field, filter, and method blanks) and duplicates (field and method duplicates). Instrument performance and stability was verified throughout analyses using matrix spikes and calibration check standards in every batch of ca. 10 samples. Further QC procedures required that blanks were below method reporting limits (MRL) and that duplicates were consistently within a 20% relative percent difference of their parent sample.
Ancillary measurements of water temperature, pH, specific conductance (SC), and dissolved oxygen (DO), and standard DOM fluorescence (FDOM; ex 325±60 nm, em 470±30 nm\(^1\); Turner Designs™ Cyclops-7™) were recorded for the Nayshkootayaow River and North Granny Creek using in situ RBR Maestro loggers, deployed in each river and set to log at a 30-minute frequency. Sensors were checked and calibrated at the beginning and end of each field campaign as a QC measure. Measurements of pH and SC were later corroborated by bench-top measurements collected prior to filtration upon returning to the on-site laboratory at the Victor Mine.

2.3.3 UV and Fluorescence Measurements

Fluorescence excitation-emission matrix (EEM) scans were measured on a Varian Cary Eclipse spectrophotometer over emission wavelengths (em) 300-550 nm, at 2 nm increments, and excitation wavelengths (ex) 240-450 nm, at 10 nm increments. Samples were measured in a 1.0 cm quartz cell (3.5 mL, Agilent), and blank EEM and Raman scans (ex 350 nm) were collected daily using ultra-pure DI water (Milli-Q®; 18.1 MΩ cm). Excitation emission matrices were corrected according to Stedmon et al. (2003) and Cory and McKnight (2005) for inner-filter effects, Raman scattering, and instrument bias. During correction, EEMs were Raman normalized and converted to Raman units (R.U., nm\(^{-1}\)). UV absorbance scans were measured on a Cary 300 UV-Vis spectrophotometer (Agilent Technologies) between 200 and 800 nm, with 1 nm increments, using DI water as the blank. Fluorescence and UV absorbance analysis was done within 30 days of sample collection and included field and method duplicates in every batch of ca. 10 samples to adhere to QA procedures. Further details regarding EEMs corrections and spectroscopic analysis performed in this study are provided in Chapter 3.3.3.

Qualitative indices of DOM composition (Table 2.1) were retrieved from corrected EEM scans and UV absorbance measurements using an existing MATLAB (MathWorks Inc.) code, adapted for the Cary Eclipse fluorometer and ex/em wavelengths used in this study (Cory and McKnight, 2005). Standard FDOM measurements for discrete water samples were

\(^1\) Excitation-emission wavelengths are followed by ± band pass values to give the full width at half maximum (FWHM)
extracted from the corrected EEM matrices generated using MATLAB code using the ex/em wavelength pair upon which the in situ Cyclops-7™ FDOM sensors were centered. Specific UV Absorbance, an indicator of DOM aromaticity, was calculated as the UV absorbance of a filtered sample at 254 nm (m\(^{-1}\)) divided by the DOC concentration and is reported in units of L mg\(^{-1}\) m\(^{-1}\) (Weishaar et al., 2003; USEPA, 2009). Fluorescence index determines whether the source of DOM is more autochthonous, with high FI values (ca. 1.8), or allochthonous, with low FI values (ca. 1.2) (McKnight et al., 2001). The FI for each sample was calculated as the ratio of two different emission intensities (470 and 520 nm), obtained at ex 370 nm (McKnight et al., 2001; Cory and McKnight, 2005). Humification index serves as an indicator of the extent of humification, where higher values indicate a greater degree of humification. The HIX value, defined as the sum of fluorescence emission intensity in the 435-480 nm region divided that of the 300-345 nm and 435-480 nm regions combined, at excitation 254 nm (Ohno, 2002). Humification index values range from 0 to 1, where higher values indicate a greater degree of humification. Utilization of parallel factor (PARAFAC) analysis was also attempted to provide more elaborate details into DOM composition, however issues encountered proved unresolvable within the scope of this thesis (see Appendix A).
Table 2.1: Definitions and calculations of DOM optical indices used in this study. Abbreviations are em = emission wavelength, and ex = excitation wavelength.

<table>
<thead>
<tr>
<th>DOM Quality Index</th>
<th>Reference</th>
<th>Calculation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific UV Absorbance (SUVA)</td>
<td>Weishaar <em>et al.</em> (2003)</td>
<td>SUVA = ( \frac{UV \text{ absorbance at } 254 \text{ nm}}{DOC \text{ concentration } (mg \text{ L}^{-1})} )</td>
<td>Provides a measure of DOM aromaticity, where higher SUVA values indicate greater aromaticity</td>
</tr>
<tr>
<td>Fluorescence Index (FI)</td>
<td>McKnight <em>et al.</em> (2001); modified by Cory and McKnight (2005)</td>
<td>FI = ( \frac{Intensity \text{ at em } 470 \text{ nm}}{Intensity \text{ at em } 520 \text{ nm} \text{ at ex } 370 \text{ nm}} )</td>
<td>Determines if the origin of DOM is more microbial (autochthonous; high FI ~1.8) or more terrestrial (allochthonous; low FI ~1.2) in nature</td>
</tr>
<tr>
<td>Humification Index (HIX)</td>
<td>Zsolnay <em>et al.</em> (1999); modified by Ohno (2002)</td>
<td>HIX = ( \frac{\sum I_{435-480}}{\sum I_{300-345} + I_{435-480}} \text{ at ex } 254 \text{ nm} )</td>
<td>Indicates degree of humification or humic substance content. Ranges from 0 to 1, with higher values indicative of a shift of the emission spectra to longer wavelengths due to lower H:C ratios, associated with greater degree of humification</td>
</tr>
</tbody>
</table>
2.3.4 Statistics and Principal Component Analysis

Statistical analyses were performed using SPSS Statistics (Version 21) software, while GraphPad Prism software was used to create additional figures. The Shapiro-Wilks’ W test was performed to assess normality on all source water optical, isotopic, and geochemical data. In cases where data were normally distributed, two-tailed paired t-tests (p = 0.05) were conducted to examine differences of means in source waters by depth and season. Where data were not normal, nonparametric Mann Whitney U (p = 0.05) tests were used instead.

Water samples collected within the 0-5 cm surface peat layer were combined in statistical treatments with samples collected from shallow (50 cm and 90 cm r.t.s.) depths for equivalent peatland types. Together, surface and shallow samples were aggregated as “Shallow” after past research and our own statistical tests suggested that the two were not geochemically different. Meanwhile, “Deep” (150 cm) pore water samples in bog, fen and fen water track were kept separate from shallow samples for further analysis due to statistically significant differences of means between them for several geochemical parameters, similar to previous research findings (Ulanowski and Branfireun, 2014). Moreover, tests for differences in means between groups confirmed that values for optical parameters in each category of source water (e.g., shallow bog, deep bog) were not significantly different between seasons (spring and summer), and values for the two seasons could therefore be combined.

Principal component analysis (PCA) was performed on the Nayshkootayaow River and North Granny Creek data to reduce the dimensionality of observed tracers into principal components (PCs), to interpret dependencies existing between tracers, and to identify which tracers were responsible for most of the variability in the original water chemistry. The PCA was conducted on the Nayshkootayaow River and North Granny Creek samples separately due to the known substantial contribution of deep groundwater to the Nayshkootayaow River and not to the North Granny Creek, and the probable skewing the PCA that would result if the two rivers were grouped together.

An assumption of PCA is that variables are linearly related, which indicates that stream chemistry is the result of conservative or physical mixing, and not of chemical reactions
within the stream (Christophersen and Hooper, 1992). Hooper (2003) suggested that conservative behaviour could be assessed using bivariate mixing plots. However, while collinearity within the bivariate plots does not necessarily confirm conservative mixing, there is no more objective method of evaluating the linearity of the mixing (Inamdar, 2011). Thus, bivariate plots were applied for the following fluvial tracers to ensure linear relationships: SUVA, FI, HIX, Laboratory FDOM, DOC, SC, Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), δ\(^{18}\)O, and δD. Ion concentrations were converted to mEq L\(^{-1}\) for PCA so that those tracers would be treated as equivalently reactive. Tracers were accepted for PCA when they had at least one linear correlation with another tracer (p < 0.01) (Barthold et al., 2011). Kaiser-Meyer-Olkin (KMO) measures of overall and individual variables were also assessed to further support the sampling adequacy of the selected set of variables, where a KMO measure of 0.6 or greater was considered acceptable. For the Nayshkootayaow River, all of the aforementioned tracers exhibited some form of collinearity (r ≥ 0.3) and were selected as conservative tracers suited for PCA, whereas for the North Granny Creek, Ca\(^{2+}\) and Cl\(^-\) exhibited no linear trends and were dismissed from the PCA. In situ FDOM measurements were excluded from both the Nayshkootayaow River and North Granny Creek PCA, as they appeared to violate the assumption of conservative mixing. As is discussed further in Chapter 3, this may have been attributed to some amount of signal quenching in situ.

With PCA, a new mixing space (U-space) is defined by the stream water chemistry that describes variability within the dataset using as few dimensions as possible. The number of PCs retained after the PCA determines the dimensions of U-space, however this can be somewhat subjective. Here, the number of PCs retained was determined by the eigenvalue-one criterion (Kaiser, 1960), visual inspection of scree plots, as well as the percentage of variance explained. Varimax orthogonal rotations were employed to facilitate the interpretation of the Nayshkootayaow River and North Granny Creek stream data points in their respective mixing spaces.
2.4 Results

2.4.1 Seasonal Variation in Hydrology and *In Situ* Water Chemistry

The 2013 study season was considerably warmer and drier than the long-term averages for the Lansdowne House meteorological station. The annual average temperature for 2013 was 3.5 °C warmer than the 1971-2000 average for the station, while average monthly temperatures between April and October were an average 4.2 °C warmer than the long-term norm. Similarly, maximum monthly temperatures were higher than normal, reaching on average about 10 °C above the norm over the course of the year.

Snowmelt began in late April, when maximum daily temperatures rose above 0 °C, and when average daily temperatures were sustained near or above freezing, promoting snowmelt and increased streamflow. Annual peak discharge in the Nayshkootayaow River occurred on May 3, 2013 (ca. 427 m$^3$ s$^{-1}$) (Figure 2.2), however this discharge value may represent an overestimation of flow as it exceeds the discharge extrapolation capabilities of the established rating curve. Annual peak discharge in the North Granny Creek occurred in the same week, on May 8, at ca. 3.14 m$^3$ s$^{-1}$. A smaller discharge peak observed between annual peak discharge and the first week of June can be attributed to spring precipitation events alongside the recession of snowmelt and meltwater contributions to streamflow. The RBR multi-channel loggers had not yet been acquired and thus could not be deployed in time to capture changes in water quality during the early freshet period, which may be considered the peak of watershed connectivity. While total freshet precipitation prior to sampling was 58.9 mm, only 3.6 mm fell during the spring sampling campaign, meaning that spring sampling was more representative of the hydrological conditions of the freshet recession.

The summer was relatively dry, with a cumulative rainfall for June, July, and August of 153 mm, compared to the 291 mm climate norm (Environment Canada, 2014). The lack of significant precipitation events throughout the summer and warm temperatures lowered the water table level in the peatland, while base flow conditions were maintained in both the Nayshkootayaow River and North Granny Creek. The average flow in the Nayshkootayaow was the lowest recorded for an extended period of time since the inception of Victor Mine in 2005 (D. Ott, De Beers Group of Companies, personal communication, 2015). Rainfall during the summer period and into the autumn consisted of scattered and typically short-
duration events, although rainfall events during this time in the area are usually longer duration and of low-intensity. Total rainfall for the late summer to autumn period (August 16\textsuperscript{th} to October 31\textsuperscript{st}) amounted to approximately 110 mm, of which 70 mm was accounted for by three distinct events. Precipitation between September and August for the area is on average 150 mm, however those months were much drier than usual in 2013, with a total of only 49 mm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hydrographs.png}
\caption{Hydrographs for the Nayshkootayaow River (top) and North Granny Creek (bottom), including discharge (blue line) and precipitation (grey bars) for the freshet (pre-study) to autumn period.}
\end{figure}

The pH and specific conductivity (SC) were notably different between the Nayshkootayaow River and North Granny Creek throughout the study period (Figure 2.3). In the Nayshkootayaow River, pH readings during spring were around 7.8, after which time they increased until their peak of pH 8.6 (July 14). After staying relatively constant at pH \textit{ca.} 8.4 for almost a month, pH decreased to a minimum in the autumn (pH 7.6). Specific conductivity in the Nayshkootayaow River ranged from 100.5 to 548.5 \(\mu\)S cm\(^{-1}\), with the
minimum value occurring during spring, and the maximum value occurring on August 5, after a steady but substantial increase. Days after peak SC was observed, a rapid decrease of \( ca. 230 \, \mu S \, cm^{-1} \) (45%) was observed in under a week. The marked decline in SC was consistent with the decrease in pH noted above and was observed alongside a summer rainfall event (3-day event, total rainfall = 15.5 mm), which was preceded by days of sporadic rainfall with less than 2.3 mm d\(^{-1}\). The rainfall event also resulted in a significant increase in discharge (0.88 to 2.90 m\(^3\) s\(^{-1}\)) in the Nayshkootayaow.

In the North Granny Creek, pH values ranged from a minimum of 6.08 during spring, to a maximum pH of 7.2 in mid-August (August 12\(^{th}\)). The increase in pH was gradual, and peak pH was observed later than the summer peak in the Nayshkootayaow River (July 15\(^{th}\)). Values for pH were only slightly lower in the autumn. The SC trend was similar to the one observed for pH, with the lowest values observed during spring (17.1 \( \mu S \, cm^{-1} \)), and the highest in mid-August (93.8 \( \mu S \, cm^{-1} \)). Specific conductivity variation in the North Granny Creek was gentle in comparison to variation in the Nayshkootayaow River, suggesting one or a number of additional SC-altering factors in the latter.

In both the North Granny Creek and the Nayshkootayaow River, DO and temperature were negatively correlated \((r = -0.83 \, \text{and} \, -0.59, \, \text{respectively,} \, p < 0.01)\), as expected since oxygen solubility increases with colder water temperatures. Dissolved oxygen concentrations were lowest during the spring and early summer (minimum 1.86 and 4.20 mg L\(^{-1}\) for the North Granny Creek and Nayshkootayaow River, respectively) and increased gradually in mid- to late July, with the highest concentrations (7.84-9.00 mg L\(^{-1}\) and 9.03-9.87 mg L\(^{-1}\), respectively) observed alongside the lowest temperatures in late October (1.4-4.6°C and 1.4-5.0 °C, respectively).

Diurnal oscillations were noted in all in situ logger measurements of surface water temperature, DO, pH, and SC. Diurnal trends were especially pronounced for DO and temperature in both rivers, and for pH in the Nayshkootayaow River. Daily maximums occurred at approximately the same time for all of the stated parameters, which was typically just prior to sunset, in the late afternoon or evening, while daily minimums were reached after sunrise, in the mid-morning.
2.4.2 Ions, Stable Isotopes of Water, DOC and DOM Quality Indices in Study Rivers and Peatland Sources

Ion concentrations varied between surface and source waters. Variations in river ion concentrations matched temporal trends in SC. This was particularly noticeable in the Nayshkootayaow River, where base cation concentrations ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Na}^+$) were markedly higher during their peak in the summer than during spring and autumn periods (summer means $\pm$ SD: $\text{Ca}^{2+} = 28.71 \pm 15.27$ mg L$^{-1}$, $\text{Mg}^{2+} = 9.48 \pm 2.47$, and $\text{Na}^+ = 34.67 \pm 15.27$) (Table 2.2). These increases were observed with the same timing as an increase in SC at that study site. In the North Granny Creek, the ion concentrations were not as varied as in the Nayshkootayaow, and the highest ion concentrations were not uniquely observed in the
summer. The highest mean and maximum concentrations of Ca$^{2+}$ (mean = 8.55 ± 0.72 mg L$^{-1}$, maximum = 9.81 mg L$^{-1}$) and Mg$^{2+}$ (mean = 1.77 ± 0.25 mg L$^{-1}$, maximum = 2.16 mg L$^{-1}$) were observed in the summer, however, the highest Na$^+$ concentrations (mean = 4.98 ± 0.15 mg L$^{-1}$, maximum = 5.22 mg L$^{-1}$) were observed in the autumn. Among the surface water sources studied, Ca$^{2+}$ and Mg$^{2+}$ concentrations were highest in deep fen (45.35 ± 19.45 mg L$^{-1}$ and 9.15 ± 4.50 mg L$^{-1}$, respectively) and in deep groundwater (clay: 71.06 ± 9.85 mg L$^{-1}$ and 13.13 ± 5.13 mg L$^{-1}$, n = 9; and bedrock: 52.69 ± 21.77 mg L$^{-1}$ and 6.86 ± 4.82 mg L$^{-1}$, n = 4) samples (Figure 2.4).

Stable isotopes of water ($\delta^{18}$O for oxygen and $\delta$D for hydrogen) differed markedly between the two rivers. Isotope values for $\delta^{18}$O and $\delta$D were more depleted in the Nayshkootayaow River than in the North Granny Creek in seasonal comparisons, and more closely resembled the Global Meteoric Water Line (GMWL) and LMWL (Figure 2.5). For both the Nayshkootayaow River and the North Granny Creek, $\delta$D and $\delta^{18}$O values were more depleted (negative) during spring than during the summer and autumn, when isotope values were more enriched (positive) and plotted below and further away from the LMWL.
Table 2.2: Dissolved organic carbon and major ion concentrations (Ca$^{2+}$, Na$^+$, Mg$^{2+}$, and Cl$^-$) for the Nayshkootayaow River and the North Granny Creek during spring recession, summer, and autumn, as well for the full study period (spring to autumn). Results are presented as the mean ± standard deviation for each flow period, with the range in parentheses.

<table>
<thead>
<tr>
<th>River and Season</th>
<th>DOC (mg L$^{-1}$)</th>
<th>Ca$^{2+}$ (mg L$^{-1}$)</th>
<th>Na$^+$ (mg L$^{-1}$)</th>
<th>Mg$^{2+}$ (mg L$^{-1}$)</th>
<th>Cl$^-$ (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nayshkootayaow River</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring (recession)</td>
<td>15.1 ± 0.3</td>
<td>13.85 ± 0.68</td>
<td>2.81 ± 0.71</td>
<td>1.81 ± 0.25</td>
<td>6.24 ± 1.67</td>
</tr>
<tr>
<td>(n = 9)</td>
<td>(14.6-15.6)</td>
<td>(12.87-14.84)</td>
<td>(1.90-3.77)</td>
<td>(1.40-2.09)</td>
<td>(3.21-8.37)</td>
</tr>
<tr>
<td>Summer</td>
<td>12.4 ± 1.4</td>
<td>28.71 ± 2.48</td>
<td>34.67 ± 15.27</td>
<td>9.48 ± 2.47</td>
<td>61.66 ± 26.23</td>
</tr>
<tr>
<td>(n = 7)</td>
<td>(10.1-14.6)</td>
<td>(25.46-31.19)</td>
<td>(17.32-49.14)</td>
<td>(5.77-11.88)</td>
<td>(27.88-88.80)</td>
</tr>
<tr>
<td>Fall</td>
<td>15.7 ± 0.5</td>
<td>15.87 ± 1.10</td>
<td>13.27 ± 0.37</td>
<td>5.21 ± 0.18</td>
<td>-</td>
</tr>
<tr>
<td>(n = 8)</td>
<td>(15.0-16.5)</td>
<td>(14.86-17.68)</td>
<td>(12.64-13.74)</td>
<td>(5.03-5.54)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Full Study Period</strong></td>
<td>14.2 ± 1.7</td>
<td>20.01 ± 7.12</td>
<td>17.81 ± 16.65</td>
<td>5.68 ± 3.62</td>
<td>35.58 ± 34.03</td>
</tr>
<tr>
<td><strong>North Granny Creek</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring (recession)</td>
<td>20.7 ± 1.3</td>
<td>5.46 ± 0.42</td>
<td>1.16 ± 0.22</td>
<td>0.52 ± 0.06</td>
<td>3.23 ± 1.80</td>
</tr>
<tr>
<td>(n = 10)</td>
<td>(18.9-22.8)</td>
<td>(5.09-6.33)</td>
<td>(0.93-1.45)</td>
<td>(0.39-0.58)</td>
<td>(1.54-6.57)</td>
</tr>
<tr>
<td>Summer</td>
<td>18.7 ± 2.4</td>
<td>8.55 ± 0.72</td>
<td>3.09 ± 0.45</td>
<td>1.77 ± 0.25</td>
<td>6.34 ± 1.52</td>
</tr>
<tr>
<td>(n = 7)</td>
<td>(15.1-22.0)</td>
<td>(7.76-9.81)</td>
<td>(2.24-4.01)</td>
<td>(1.17-2.16)</td>
<td>(4.80-9.55)</td>
</tr>
<tr>
<td>Fall</td>
<td>16.8 ± 0.5</td>
<td>4.73 ± 0.90</td>
<td>4.98 ± 0.15</td>
<td>1.17 ± 0.08</td>
<td>-</td>
</tr>
<tr>
<td>(n = 8)</td>
<td>(16.3-17.6)</td>
<td>(3.70-5.83)</td>
<td>(4.78-5.22)</td>
<td>(1.04-1.29)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Full Study Period</strong></td>
<td>18.8 ± 2.2</td>
<td>6.49 ± 1.86</td>
<td>3.00 ± 1.54</td>
<td>1.20 ± 0.57</td>
<td>4.96 ± 2.25</td>
</tr>
</tbody>
</table>
Figure 2.4: Box and whisker plots of water chemistry values and concentrations (Ca\(^{2+}\), Mg\(^{2+}\), SC, and DOC) and optical indices (SUVA, FI, laboratory measured FDOM, and HIX) for source waters (shallow (S) and deep (D) bog, fen, and fen water track (FWT) pore waters, and clay (Cl) and bedrock (Bdr) groundwaters (GW)), and the two study streams, the Nayshkootayaow River (NR) and the North Granny Creek (NGC). Source water samples were collected during distinct sampling days in the spring and autumn, and results were aggregated for each respective box and whisker plot. Box and whisker plots for the NR and NGC are aggregates of results from discrete sampling throughout.
the spring, summer, and autumn sampling campaigns. The line within each box indicates the median, and the boxes are bound by the 25th and 75th percentiles. The Tukey method was used to plot whiskers and outliers for the box plots (grey circles).

Figure 2.5: Stable isotopes of water (δD and δ¹⁸O, ‰ VSMOW) of the North Granny Creek (NGC) (triangles) and Nayshkootayaow River (NR) (circles), grouped by season. Solid and dashed lines represent the Global and Local Meteoric Water Lines (GMWL and LMWL, respectively), where the LMWL was generated using rain and snow samples collected within 15 km of the De Beers Victor Mine between 2008 and 2013.

Dissolved organic carbon concentrations, as well as DOM spectroscopic indices varied depending on the study river (Nayshkootayaow River or North Granny Creek) and sample date. Concentrations of DOC in the North Granny Creek (18.8 ± 2.2 mg L⁻¹, n = 25) remained higher than in the Nayshkootayaow River (14.2 ± 1.7 mg L⁻¹, n = 24) throughout the study period (Table 2.2). The overall trends in DOC in both streams were similar, but appeared less variable in the Nayshkootayaow (Figure 2.6). Peak DOC in the North Granny Creek was observed in the spring (22.8 mg L⁻¹), while the minimum DOC concentration was observed in the autumn (16.3 mg L⁻¹), with the exception of an outlying minimum on August 9th (15.2 mg L⁻¹). In the Nayshkootayaow River, spring and fall DOC concentrations
were comparably high (mean = 15.1 ± 0.3 mg L⁻¹ and 15.7 ± 0.5 mg L⁻¹, respectively), while the minimum DOC concentration was observed in the summer (11.5 mg L⁻¹), with an outlying minimum again being observed on August 9th (10.1 mg L⁻¹). Dissolved organic carbon concentrations were highest in shallow bog samples (40.6 ± 13.8 mg L⁻¹), however river concentrations were more comparable to shallow fen (17.7 ± 6.7 mg L⁻¹), deep fen (12.2 ± 3.8 mg L⁻¹), and clay groundwaters (15.2 ± 3.6 mg L⁻¹).

Values of SUVA and FI decreased and increased, respectively, from June to late October in both rivers (Figure 2.6). In the North Granny Creek, SUVA values were slightly higher than in the Nayshkootayaow River, while FI values were just below those of the Nayshkootayaow River. Specific UV absorbance decreased with time in both the North Granny Creek and Nayshkootayaow River, with the highest measurements generally observed during spring (maxima = 2.19 and 1.98 L mg⁻¹ m⁻¹, respectively) and the lowest, observed in the autumn (minima = 1.43 and 1.53 L mg⁻¹ m⁻¹). However, local SUVA maxima (2.13 and 2.15 L mg⁻¹ m⁻¹) were noted in both rivers after the same 3-day summer rainfall event described above (total rainfall = 15.5 mm). This response was rapid and momentary, and was observed alongside a decrease in DOC. Specific UV absorbance values averaged 1.74 (±0.17) and 1.84 (±0.25) L mg⁻¹ m⁻¹ in the Nayshkootayaow River and the North Granny Creek. Deep groundwaters, collected from bedrock and clay aquifers, generally had the lowest SUVA values (1.25 ± 0.34 L mg⁻¹ m⁻¹ and 1.27 ± 0.18 L mg⁻¹ m⁻¹, respectively). A greater range in SUVA values was observed in fen waters (1.14-2.69 L mg⁻¹ m⁻¹, n = 18), relative to other peatland types, exhibiting both comparable and lower values than bog (1.80-2.37 L mg⁻¹ m⁻¹, n = 17) and fen water track (1.76-2.59 L mg⁻¹ m⁻¹, n = 12) waters. Both rivers had SUVA values in the same range as fen waters, slightly lower than those of other peatland waters and above those observed for deep groundwaters.

Fluorescence index values increased from minima of FI = 1.20 (Nayshkootayaow) and 1.13 (North Granny Creek) during spring recession into August. Meanwhile, although maximum FI values were observed in the autumn for both the Nayshkootayaow and the North Granny Creek (FI = 1.33 and 1.26), there was no significant difference in FI values between samples collected at the beginning of August and onwards (independent t-test, p = 0.192 and p = 0.832, respectively). Fluorescence index values averaged 1.28 (±0.03) and 1.21 (±0.04) in the Nayshkootayaow River and the North Granny Creek, respectively. Fluorescence index values
increased with depth within bog (1.02-1.42; n = 20), fen water track (1.08-1.36; n = 13), and fen waters (1.13-1.51; n = 17), while deep groundwater samples offered the highest FI values (1.28-1.62; n = 13) (Figure 2.4). River FI values were within the range of surficial and deep peatland waters. Meanwhile, the Nayshkootayaow FI values were slightly above those of the North Granny Creek, approaching those of deep bedrock groundwater.

Figure 2.6: Temporal changes in dissolved organic carbon (DOC) concentration, fluorescent dissolved organic matter (FDOM) measurements, spectroscopic indices (FI, SUVA, HIX) for the Nayshkootayaow River (black circles and line) and the North Granny Creek (white circles or grey line).

Humification index values were relatively high, averaging 0.954 (±0.016) in the Nayshkootayaow and 0.948 (±0.023) in the North Granny Creek. These values were on par with surficial peatland waters, and towards the upper end or greater than deep peatland waters and deeper groundwaters. Maximum HIX values were observed in the summer (0.973 and 0.977, respectively), while minimum values (0.918 and 0.880) were observed during summer base flow conditions for both rivers (Figure 2.6). For surface water sources, HIX
values were generally lower at depth than at the surface for bog, fen water track, and fen waters. However, although HIX values for deep clay and bedrock groundwaters varied more widely than other contributing source water types (0.90 ± 0.04, n = 13), they were among the lowest.

2.4.3 Principal Component Analysis (PCA) on Water Quality Concentrations and DOM Quality Indices

In the PCA performed for the Nayshkootayaow River, two PCs with eigenvalues greater than one were identified, explaining 70.9% and 20.4% of the variability in stream chemistry, respectively. The first component (PC1NR) was positively correlated with \( \text{Ca}^{2+} \), \( \text{Na}^{+} \), \( \text{Cl}^{-} \), \( \text{Mg}^{2+} \), and SC and negatively correlated with laboratory measurements of FDOM, DOC and HIX (see Appendix B). The second PC (PC2NR) was positively and most strongly correlated with \( \delta D \), and slightly less so with FI, while being negatively correlated to SUVA. For the North Granny Creek, two acceptable PCs were again recognized, with PC1NGC accounting for 70.4% and PC2NGC accounting for 19.8% of stream chemistry variance. Similar to the PC1NR, PC1NGC was strongly correlated with FDOM and DOC, however SUVA also shared a positive correlation. The PC2NGC differed from that in the Nayshkootayaow River, with the strongest positive correlations occurring with \( \text{Mg}^{2+} \) and SC, as well as with \( \delta^{18} \text{O} \) (see Appendix B).

Plotting the first two PCs against each other allowed us to interpret differences in source water contributions to each river according to season (Figure 2.7). Stream chemistry in the Nayshkootayaow River and North Granny Creek varied by season, as further demonstrated by distinct clustering in rotated U-space. Tracer component correlations plotted into U-space separated mixing space quadrants intuitively, representing tracers with similar associated origins; grouped into organic-rich peatland and inorganic, deep groundwater sources. In the Nayshkootayaow River, tracers associated with the peatland organic signal (SUVA, FDOM, DOC, HIX) plotted in quadrant 3, while those related to a deeper groundwater signal and evaporation effects (SC, \( \text{Mg}^{2+} \), \( \text{Na}^{+} \), \( \text{Ca}^{2+} \), \( \text{Cl}^{-} \), \( \delta^{18} \text{O} \) and \( \delta D \)) occupied the opposite quadrant 1. The identical sets of tracers separated the North Granny Creek U-space, with the organic tracers lying in quadrant 2, and the inorganic in quadrant 4. Plotting the first two PCs against each other for each site facilitated the interpretation of changes in source water contribution to streamflow over time.
Spring data from the Nayshkootayaow River plotted in a relatively tight cluster in quadrant 3, where the peatland signal explained most of the variability. For summer base flow conditions, stream chemistry received greater inputs from inorganic groundwater sources and was either markedly influenced by evaporation or mixed with evaporated waters, grouping around PC1_{NR} in quadrants 1 and 2. The signal changed again in the autumn, as exhibited by data plotting in quadrant 4, mixing inorganic and organic signals. In the North Granny Creek, spring data could be explained by a greater allochthonous organic or humic-like signal, with progressively more mixing occurring. In the summer and autumn, this transitioned to a greater inorganic (or protein-like) signal subjected to increased evaporation. In both the Nayshkootayaow River and North Granny Creek, summer data occupied a broader band of PCA mixing space, compared to tightly clustered spring and autumn data.
Figure 2.7: Results of principal component analysis (PCA) after Varimax rotation of the mixing space (U-space). Stream data points for the Nayshkootayaow River (left) and the North Granny Creek (right) are projected to evaluate differences in source water and tracer contributions to the respective stream chemistry over time (spring, summer, and autumn). Ellipses are used to identify each seasonal grouping and are for illustrative purposes only. Arrows provide the conceptual transition between seasons, with the dashed blue line represents the transition over the winter season, which was not sampled. Tracer vectors are also projected to demonstrate the strength of correlation with each principal component axis.
2.5 Discussion

2.5.1 Climate, Streamflow and Hydrological Connectivity

The warmer than normal temperatures and low precipitation made the 2013 study season a considerably dry one, even compared to a previous study in the region that noted 2010 as warmer and drier than normal (Orlova and Branfireun, 2014). As noted by Orlova and Branfireun (2014) for 2010, the dry conditions observed in 2013 may mean that results of analyses may be more applicable and relevant to the warmer and drier conditions predicted by climate change scenarios for the area.

The lack of significant precipitation and warm temperatures following spring recession resulted in base flow conditions in the Nayshkootayaow and the North Granny Creek throughout the summer. With such conditions, the fluvial network was relatively less connected than in the spring, and the groundwater fraction in the Nayshkootayaow River became much more substantial. In the late summer and autumn, water levels rose only slightly in the North Granny Creek and Nayshkootayaow River in response to increased precipitation, but were still largely supplemented by groundwater in both rivers.

The dry and warm conditions throughout the summer led to extensive peat drying, and late summer and autumn precipitation would have gone mostly to peatland storage. As peatlands dry out and they become more disconnected, as a consequence of lower water availability and decreased flow, the amount of available storage increases and more and larger rain events are required to satisfy a threshold moisture deficit and, thus reconnect peatland landscape units with the fluvial network (Quinton and Roulet, 1998; Ulanowski and Branfireun, 2014). Otherwise, diffuse groundwater flow is the only means of maintaining connectivity between the landscape and surface waters (Ulanowski and Branfireun, 2014). In additional physical observations of the downstream Nayshkootayaow River banks and riparian area, contributing rivulets and shallow macropore flow pathways (soil pipes) stopped contributing to flow as the peatland dried out. This further supports a decrease in hydrological connectivity or hydrological disconnect with peatland features. However, Kline and Branfireun (2014) also suggested that during very dry periods, flow from a fen to a river
becomes relatively more channelized, being directed by rivulets, and largely bypasses the riparian zone, while pipe flow may cease due to insufficient storage in riparian depressions.

2.5.2 Source Water Chemistry

The composition of different source waters and their respective contributions to streamflow impacts the surface water chemistry both spatially (between river orders) and temporally. The DOC concentrations in peatland pore waters found in this study were within the range of 10 to 80 mg L\(^{-1}\) reported for most northern peatlands (Blodau, 2002). Concentrations for bog sites were higher than for fen sites, an occurrence that has been commonly observed in other northern peatlands, as well as in the HBL (Moore, 1988; Reeve et al., 1996; Fellman et al., 2008; Ulanowski and Branfireun, 2013; Tfaily et al., 2015). Moreover, DOC concentrations in bog, fen water track, and fen sites in this study decreased with depth, similar to observations made by Fraser et al. (2001) in a bog in Eastern Ontario, Canada. These common observations suggest differences in the production, decomposition, and hence the quality of DOM with depth within a peatland as well as between peatland types.

Differences in DOM quality between peatland types result from dissimilarities in their efficiency of organic matter decomposition and movement of DOM. Fen vegetation provides a well-oxygenated rhizosphere, where labile DOM can be produced and which supports microbial respiration (Chanton et al., 2008; Tfaily et al., 2013). In bogs, the low hydraulic conductivity, absence of an aerated rhizosphere, and dominance of lignin-rich Sphagnum species contributed to an accumulation of more recalcitrant DOC than in fens in our study, which has been regularly reported elsewhere (e.g., Chanton et al., 1995; Chanton et al., 2008; Fellman et al., 2008). Fluorescence index generally increased from bog to fen (e.g., ca. 1.1 for shallow bog; ca. 1.3 for shallow fen), while aromaticity (SUVA) at fen sites was slightly lower than for bogs. Together, these results reflect the increased hydrological connectivity, presence of more biologically available DOM, and greater microbial degradation occurring along the ombrotrophic to minerotrophic gradient.

These results show that aromaticity, as indicated by SUVA, did not change substantially between shallow and deep peat pore waters in any of the peatland types. The degree of humification was also higher in the surface peat than at depth, while FI increased with depth in bog, fen water track, and fen pore waters. Tfaily et al. (2015) suggested that the observed
decrease in SUVA and HIX values with depth in bog and fen sites could be ascribed to the production of microbially derived DOM produced during the microbial degradation of humic and plant-derived DOM. This notion was supported by the observation of higher FI values at depth at our sites. The degradation of lignin in plant matter has also been shown to increase HIX values (Kalbitz et al., 2006), and accordingly, HIX has often been shown to be greater at the surface of various soil profiles (Inamdar et al., 2012; Klotzbücher et al., 2012). As has been widely observed in previous peatland studies (Chanton et al., 1995; Fraser et al., 2001; Fellman et al., 2008; D’Andrilli et al., 2010; Tfaily et al., 2015), our results suggest that DOM in bog, fen water track, and fen peat profiles becomes older and more microbially degraded with depth, and thus DOM that is allochthonous at the peat surface takes on an increasingly autochthonous quality with depth. Fraser et al. (2001) for instance found that DOM exported from an ombrotrophic bog changed from more allochthonous to autochthonous in character with increasing depth, with FI increasing from ca. 1.1 at 0 m peat depth to ca. 1.6 at 4.5 m. Moreover, while our results indicated a more significant decrease in HIX with depth in fen than in bog, HIX changed the most with depth in fen water track DOM. This more pronounced change in HIX might be linked to the development of fen water tracks in areas of lateral flow, as well as the high hydraulic conductivity of the characteristic shallow pools and upper 1 m of peat, and reduced hydraulic conductivity in the decomposed peat that underlies them (Leclair, 2015). Fen water tracks may therefore develop a starker stratification of peats with different degrees of microbial degradation. In contrast, the upwards and downwards hydraulic gradients in fens and bogs, respectively, may lead to a subtler stratification.

Aromaticity, DOC concentrations, and HIX values were among the lowest in the deep groundwaters (clay and bedrock) sampled in our study, which aligned with observations made in studies of boreal and arctic regions (O'Donnell et al., 2010; Inamdar et al., 2011; Inamdar et al., 2012). Fluorescence index was also highest in deep groundwater samples, at ca. 1.5, indicating more autochthonous organic matter content at such depths. The lower aromatic content in deeper groundwater flow paths has been attributed to the removal and/or alteration of those fractions by physical sorption in mineral soils and microbial processes over long residence times (Cronan and Aiken, 1985; Qualls and Haines, 1991; Inamdar et al., 2012), or simply through lower inputs of terrestrial DOM components (Balcarczyk et al.,
Additionally, in the HBL, the vertical exchange of water and solutes between the peat and low-permeability mineral substratum is thought to be negligible (Ulanowski and Branfireun, 2014). Therefore, we propose that the decrease in SUVA, DOC, and HIX, and increase in FI observed in deep groundwaters in our study was likely attributed to minimal or absent inputs of humic, aromatic autochthonous DOM and most of all, the presence of highly processed microbial DOM from the deep groundwater sources.

### 2.5.3 Seasonality of Surface Water DOM Sources, Processes, and Quality

Throughout the 2013 study period, DOC concentration and DOM composition varied considerably; changes that were supported by ancillary water chemistry (pH, SC, stable isotopes of water, and base cation concentrations). Diurnal changes in temperature, DO, pH, and SC throughout the study period were consistent with changes resulting from in-stream aquatic photosynthesis and respiration (e.g., Spencer et al., 2007). Similar to observations made by Spencer et al. (2007), minima and maxima of in situ FDOM measurements were nonconcurrent, with the highest values observed in the morning, and lowest values observed in the late afternoon. The diurnal changes in FDOM are likely attributable to a combination of microbial metabolism of DOM, photodegradation, as well as changes in the ancillary chemistry that may affect FDOM (Ibid.).

Snowmelt, precipitation events, and increased runoff during the spring led to a flushing of high concentrations of allochthonous DOM in both the Nayshkootayaow River and the North Granny Creek. In the Nayshkootayaow River, it is speculated that maximum DOC concentrations would actually have been observed before sampling began, as peak discharge was recorded approximately one month before the first sampling campaign and a large pool of DOM would presumably have been mobilized to the Nayshkootayaow during this time. Observed DOC concentrations when sampling began were still relatively high for the river. Meanwhile, peak DOC concentrations were observed in the North Granny Creek following a relatively large spring rainfall event.

Spring DOM in our study rivers was also quite different in composition and bioavailability from DOM in the summer and autumn. In our study rivers, spring DOM was characterized by peak SUVA and HIX values, as well as the lowest FI values (Figure 2.6), suggesting
dominantly high molecular weight allochthonous DOM, rich in aromatic, humic substances. Similar observations of peak DOC and SUVA values, and minimum FI during spring recession have been widely documented in other northern rivers (Neff et al., 2006; Spencer et al., 2008; Spencer et al., 2009; O'Donnell et al., 2010; Mann et al., 2012). Mann et al. (2012) noted maximum concentrations of highly aromatic allochthonous DOC (14.2 mg L\(^{-1}\)) derived from thawing surface organic matter only a few days prior to peak discharge during freshet in a large Arctic river, at concentrations comparable to those in the Nayshkootayaow in spring (15.6 mg L\(^{-1}\)). It was also suggested that although highly aromatic, the allochthonous DOM mobilized during freshet is exceptionally bioavailable over short timescales, likely owing to its freshness and limited degradation history (Mann et al., 2012). Furthermore, in the Nayshkootayaow and North Granny Creek, the depleted (more negative) isotopic signatures (\(\delta^{18}O\) and \(\delta D\)) and similarity of \(\delta^{18}O\) and \(\delta D\) to the LMWL during spring supported a dominance of snowmelt contributions to runoff and indicate that source waters had experienced very little evaporation.

Post-freshet, the decrease in SUVA and increase in FI implied a shift in the source of DOM, from young surface DOM to deeper sources contributing older, less aromatic, and more autochthonous-like DOM to surface waters in the summer (Neff et al., 2006; Spencer et al., 2009; Dittman et al., 2010; Mann et al., 2012). As a result of the dry summer conditions, hydrological flow paths deepened and relatively greater contribution from deep peat layers contributed to the North Granny Creek. Dissolved organic carbon concentrations continued to be higher in the North Granny Creek than in the Nayshkootayaow River due to the organic peatland setting of its streambed. However, in the North Granny Creek, DOC decreased from spring concentrations, while SC increased, consistent with the lower DOC concentrations and higher base cation concentrations measured in deep compared to shallow peats. Although matching the actual temporal trend, sharper decreases in HIX and SUVA, and increase in FI were observed within a relatively short period (10 days) at the beginning of August in the North Granny Creek when there was minor precipitation (Figure 2.6). The precipitation falling directly or flowing as runoff into the stream may have diluted DOM in the stream water, or caused notable mixing with deep peat pore waters.

In the Nayshkootayaow River, DOM during summer base flow conditions became more autochthonous in character. Fluorescence index increased alongside decreases in SUVA and
DOC highlighting a growing dominance of deep groundwater inputs, increased residence time of DOM in the deeper waters, and therefore greater microbial degradation (Striegl et al., 2005). Mann et al. (2012) also noted that DOM was more photochemically recalcitrant due to a greater aromaticity during the late summer months than spring recession, but also less bioavailable, perhaps as a result of remineralization of labile C from groundwater inputs. In the Nayshkootayaow, increasing SC and pH, and their peak in mid-summer aligned with peak base cation concentrations, supporting the influence of groundwater from bedrock and deep limestone aquifers at the height of summer base flow conditions. While dry conditions in the Nayshkootayaow facilitated buildup of Ca$^{2+}$ in the river water due to the calcium-rich karstic bedrock setting, as well as an increase in SC, the sharp decrease of ca. 45% in SC aligned with a relatively small 3-day precipitation event (ca. 15.5 mm) that led to more than doubling of river discharge. This indicates that during exceptionally low base flows, even small rainfall events may have a substantial effect on stream water chemistry in groundwater-dominated rivers like the Nayshkootayaow. The enriched $\delta^{18}$O and $\delta$D relative to the LMWL in both rivers reflected the dry conditions and elevated evaporation rates in the surface waters and their sources, especially in the North Granny Creek.

The temporal changes in DOM characteristics in both rivers may also suggest increased mixing of autochthonous and allochthonous-like sources or selective removal of young DOM by in-stream processing over time (Neff et al., 2006). Similar to the findings of O'Donnell et al. (2010), river FI values increased from spring to summer base flow, and into the autumn. We observed higher FI values in deep peatland and deep groundwater sources (Figure 2.4), indicating improved mixing between deeper terrestrial and microbially degraded sources of DOM in the Nayshkootayaow and North Granny Creek in the late summer and autumn. Between the beginning of August and the end of sampling in autumn in the North Granny Creek, there was very little change in FI (ca. 1.25), supporting a relatively constant allochthonous source during that time, as would be expected for a peatland stream. Meanwhile, in the Nayshkootayaow River, FI values continually increased alongside decreasing SUVA indicating that river waters were becoming more influenced by in-stream microbial processes, and less so by aromatic terrigenous DOM with time. Specifically, the rise in FI values in the Nayshkootayaow aligned with extremely low flows and visible extensive periphyton growth in the river in the autumn, which would have stimulated
microbial processing and release of autochthonous DOM (Bertilsson and Jones, 2003; Vazquez et al., 2010; Inamdar et al., 2011).

Variations in DOM optical indices and DOC concentration in the Nayshkootayaow River complemented those observed in the North Granny Creek, with the exception of autumn DOC concentrations. Average autumn DOC concentrations in the North Granny Creek were the lowest for the study period, while in the Nayshkootayaow River, concentrations rose above the high concentrations observed in the spring. Meanwhile, Nayshkootayaow River SUVA and FI values were generally lower and higher, respectively, than in the North Granny Creek throughout the study period. These findings agree with those of Creed et al. (2015), who attributed the decrease in SUVA with increasing stream order to a shift from aromatic to aliphatic (less complex) DOM, from low to higher order streams. Creed et al. (2015) also found that higher order rivers were more influenced by autochthonous DOM than were lower order streams, and thus have higher FI values, largely because of the preferential loss of aromatic DOM en route from terrestrial sources and greater microbial activity. The difference in the dominance of allochthonous inputs and primary production according to stream order has long been established. In a boreal watershed in Quebec, Conners and Naiman (1984) showed that ca. 90% of DOM in headwater streams (1st and 2nd order) was terrestrially derived, while in higher order streams (> 5th order), ca. 90% of DOM was autochthonous due to increased production by macrophytes and periphyton. Indeed, the increased predominance of autochthonous DOM with increasing stream order is a fundamental principal of the river continuum concept (Vannote et al., 1980; Thorp and Delong, 2002; Creed et al., 2015), and holds true in the northern peatland environment studied herein.

Studies have shown a positive correlation between HIX and DOM aromaticity (Kalbitz et al., 2003), however differences observed in HIX and SUVA in the Nayshkootayaow River and North Granny Creek would suggest that there are likely differences in the origins, release mechanisms and/or kinetics involved in HIX and SUVA characteristics, as put forth by Inamdar et al. (2011). For instance, the release of humic DOM into stream runoff has been tied to fluctuations in groundwater elevation (Inamdar et al., 2011), while in-stream biomass degradation could selectively remove young, labile DOM, and release more humified content to increase HIX (Neff et al., 2006; Hunt and Ohno, 2007). Additionally, the autochthonous labile DOM derived from periphyton is less colored than allochthonous DOM and therefore
may not absorb at certain UV wavelengths (Scully et al., 2004), and may not fluoresce. However, DOM from periphyton is rapidly assimilated by bacteria (Bertilsson and Jones, 2003), and microbial or bacterial utilization of non-fluorescent algal-derived DOM has been found to result in the production of fluorescent DOM (Rochelle-Newall and Fisher, 2002). Therefore, increased relative inputs of autochthonous DOM would still increase fluorescence as well as FI, which are measured at higher wavelengths than SUVA. Correspondingly, the contribution of bioavailable DOM from periphyton in late summer and autumn in the Nayshkootayaow River may explain the simultaneous decrease in SUVA and increases in DOC concentrations and in situ FDOM measurements that were observed. Primary production accounts for a high proportion of total carbon input in rivers and streams (estimated at between 40-80%), and hence likely DOM inputs as well (Bertilsson and Jones, 2003; Singh et al., 2013).

During the dry summer and autumn when the peatlands are expected to be largely decoupled from higher order rivers, the substantial groundwater inputs and base flow dominated conditions in these rivers, and optimal conditions external to them (e.g., oxygen availability, shallow flow allowing deeper light penetration) would have the potential to foster DOM-altering primary productivity. In addition, the low flow conditions would have allowed increased light penetration in the river and more extensive photodegradation of allochthonous DOM (Del Castillo, 2005; Koehler et al., 2012), compared to autochthonous DOM, which is less sensitive to photodegradation (Moran and Covert, 2003). Photochemical decomposition of aromatic humic organic matter has been shown to transform these typically recalcitrant substances into DOM that is readily metabolized by bacteria (Wetzel et al., 1995), and may therefore promote autochthonous DOM production. Considering that groundwater inputs to the Nayshkootayaow River have been previously estimated at ca. 45% during the low flow conditions (Orlova and Branfireun, 2014), that conditions intrinsic and extrinsic to the river during that time are favorable to photo- and biodegradation, and that these processes supply autochthonous DOM in-stream, we propose that upwards of 45% of river DOM during low flow is autochthonous in the Nayshkootayaow.
2.5.4 Seasonal Variability in Principal Component Analysis

Using base ion chemistry, stable isotopes of water, and DOM quality and concentration with PCA, the relative importance of shallow and deep peat pore waters and deep groundwater on streamflow generation in each season could be interpreted. Although PCA was done separately on the Nayshkootayaow and the North Granny Creek, data clustered distinctively and fairly intuitively by season in both PCA mixing spaces, indicating that the influence of each source water type varied by season (Figure 2.7). In both rivers during spring, allochthonous aromatic DOM was among the most important DOM inputs to the river chemistry. Spring recession data for the Nayshkootayaow River and North Granny Creek plotted uniquely in quadrants 3 and 2 of their respective mixing spaces, when shallow allochthonous pore water and meltwater with high DOC concentration and humic-like fluorescence properties were the dominant contributors. Summer data from the Nayshkootayaow River clustered around the positive end of PC1NR, indicating that the river was enriched in base cations (Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Cl\(^-\)), and that SC and \(\delta^{18}\)O were highly important to variability in the stream associated with deep groundwater and deeper fen waters during base flow. Dissolved organic carbon concentrations became less important to the water quality variability during that time, due to the low DOM content of the contributing groundwaters. Likewise, changes in summer data in the North Granny Creek were increasingly influenced by base cation chemistry, \(\delta^{18}\)O, and SC, however humic-like fluorescence and DOC concentration continued to affect the water quality variability. This can be explained by deeper sources contributing during the base flow period in the North Granny Creek, and that these sources were persistently peatland-derived. In the autumn in the Nayshkootayaow, variability was described by influences of microbial metabolism, periphyton growth, and continuing contributions of deep groundwater. Deeper groundwater sources generally have low DOC concentrations (Striegl et al., 2007) and have been shown to decrease terrestrial characteristics of DOM through enhanced microbial processing of allochthonous DOM and subsequent contribution of autochthonous DOM (O'Donnell et al., 2010). Therefore, FI, measuring the relative contribution of allochthonous and autochthonous sources, became more important to the variability of the river chemistry in the Nayshkootayaow River as well as in the North Granny Creek in the autumn. This highlighted the importance of bioavailability and rapid microbial utilization of DOM from deeper watershed sources into more protein-like molecules. Similar results were obtained by
Inamdar et al. (2012), who found that protein-like fluorescence and FI were important in discriminating between deep DOM sources in PC mixing space.

The PCA results show that organic and inorganic sources can be distinguished by evaluating DOM quality and concentration indices alongside ancillary source water tracers, and that seasonal changes in these sources influenced water quality variability in both rivers. It is possible that by further breaking down DOM into better defined PARAFAC components (Cory and McKnight, 2005), PCA might prove to be a more useful explanatory tool, since those components have been linked to very specific attributes of source waters and of DOM processing. For instance, Balcarczyk et al. (2009) included PARAFAC components in PCA and were able to recognize photodegradation in thermokarst DOM. However, our results indicate that even simple DOM quality measurements may have the power to elucidate the relative contributions of source waters throughout the ice-free season in the HBL. Orlova and Branfireun (2014) used end-member mixing analyses (EMMA) without DOM quality indices or concentrations to estimate the proportions of groundwater, surface water and precipitation contributing to the Nayshkootayaow River and several of its tributaries during wet and dry periods. With additional DOM quality tracers, this PCA data may become more definitive, given that FDOM was the most influential tracer to PC1_{NR} and PC1_{NGC} in our study. Moreover, with the capability to continuously monitor FDOM in situ, there is a strong potential for the proportions of source waters and their optical properties to be tracked continuously as well.

2.6 Conclusion

The source and composition of DOM in the North Granny Creek and Nayshkootayaow River was considerably varied on both spatial and temporal scales, with apparent differences in stream order and throughout the study period. Dissolved organic matter is known to increase in autochthonous character in higher stream orders as primary production becomes more prevalent (Vannote et al., 1980; Thorp and Delong, 2002), and our study was no exception. However, our results also show that different factors control the quantity and quality of DOM in a channel, particularly in higher order northern peatland rivers such as the Nayshkootayaow. The influences controlling DOM quality and concentration vary from spring to fall, and with changing flow condition and contributing source waters, as has been
demonstrated in previous studies (Neff et al., 2006; Spencer et al., 2008; O'Donnell et al., 2010; Inamdar et al., 2011; Mann et al., 2012; Singh et al., 2013). Changes in the composition of riverine DOM are tied to inherent variations in DOM properties, including bioavailability (Del Giorgio and Davis, 2003; Guillemette and del Giorgio, 2011; Mann et al., 2012) and capacity for the complexation and transport of metals, such as Hg (Aiken et al., 2011). This can have important implications towards the uptake and efficient transfer of Hg to fish, and other aquatic life. In the Nayshkootayaow River, we observed a shift from predominantly terrestrially derived DOM during spring snowmelt recession to increased mixing with autochthonously produced DOM during dry conditions in the summer and autumn. High proportions of groundwater inputs and unanticipated levels of primary production during low flows late in the summer and autumn fueled microbial processing (Bertilsson and Jones, 2003) and led to non-conservative mixing of DOM from allochthonous and autochthonous sources. It follows that, in channels interacting with relatively labile groundwaters and during periods of disconnection from the peatland landscape, it would be inadvisable to use DOM quantity or quality as a representative measure of peatland carbon or DOM during those periods. Using measures of DOM quality from these higher order rivers for peatland mass balances may reflect DOM resulting from in-stream primary production and microbial processes, rather than entirely from those occurring in the peatland, especially during base flow, when groundwater is a dominant contributor. The conditions observed during the summer and autumn periods were much drier than are typical for the region, and such in-stream production is considered an unusual occurrence because of this. However, extreme dry conditions are likely to become more common with climate change (Roulet, 1991; Hengeveld, 2000), and therefore the observation of in-stream production may be reflective of future surface water productivity. The contrasting trends in DOM concentration and quality from spring to autumn suggest that it would be difficult to interpret an annual mass balance of carbon or DOM for the peatland landscape based solely on the quantity or quality of DOM in higher order channels, as the source is neither constant nor predictable. The amount of carbon may be misrepresented by measurements of quality in high order rivers, such as the Nayshkootayaow, leading to a potential underestimation of the carbon exports in the organic matter budget. Conversely, Nayshkootayaow River DOM appears to be most representative of actual peatland-derived DOM during the traditionally undersampled freshet period. Dissolved organic matter
chemistry from a summation of first-order streams, similar to the North Granny Creek, would likely be more useful in peatland chemical mass balances, since source waters would be consistently peat-derived throughout the ice-free period.

Furthermore, in the PCAs for both the North Granny Creek and the Nayshkootayaow River, out of all identified tracers, laboratory measurements of FDOM and DOC explained much of the variability of stream chemistry. This suggests that with an uninterrupted signal, continuous FDOM measurements have the potential to serve as a continuous indicator of DOM movement from peatland headwater streams to higher order rivers. In streams where a relationship between concentration and FDOM is established, the continuous measurement of FDOM may serve as an adequate tool for estimating the DOM concentration and carbon budget of the northern peatland landscape of the HBL.
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CHAPTER 3

3 Optical measurements as proxies for dissolved organic carbon and mercury in subarctic streams and rivers

3.1 Introduction

Natural dissolved organic matter (DOM) is a complex, heterogeneous mixture of high to low molecular weight organic molecules, and an important form of organic matter in all natural waters. Dissolved organic matter is dynamic, varying in both quantity and quality over time and across ecosystems, and plays a significant role in water quality and aquatic biogeochemical processes. In wetlands and riverine surface waters, colored DOM can decrease light penetration through the water column (Markager and Vincent, 2000), as well as support aquatic ecosystem metabolism (Wetzel, 1984). Perhaps most importantly, DOM plays a key role in the cycling of carbon and other elements in aquatic environments (Wetzel, 1995; Kayranli et al., 2010). The composition and quality of aquatic DOM differ according to its source, and influence its bioavailability, solubility, and overall function in the environment (Aiken, 2014). Broadly, DOM is classified as being derived either from algal and microbial processes occurring within the aquatic system of study (autochthonous), such as grazing, cellular release, organic matter degradation, and algal senescence, or from soils and plant material produced in external terrestrial environments and transported to the aquatic system (allochthonous). Approximately 50% of DOM is carbon (C) by mass, so DOM concentration is typically measured analytically as dissolved organic carbon (DOC) (Mitsch and Gosselink, 2007; Cory et al., 2011). However, due to its changeable and complex chemistry, the actual composition of DOM is difficult to characterize.

Dissolved organic matter is also generally known to contain important chemical structures such as thiols, with reduced sulfur binding sites that are very effective, and very strong binding ligands (Dyrssen and Wedborg, 1991; Xia et al., 1999; Skyllberg et al., 2000). Dissolved organic matter is thus involved in the complexation and availability of trace metals such as mercury (Hg) (Reuter and Perdue, 1977; Driscoll et al., 1995; Aiken et al., 2011; Baken et al., 2011), and the mobilization of other pollutants (Chin et al., 1998; Baker and Curry, 2004), since the complexation of heavy metals with DOM in the environment enhances the solubility and transport of these solutes (Buffle, 1988; Aiken, 2014). Mercury is
a global contaminant that is derived from natural and anthropogenic sources. Anthropogenic sources, which have increased the amount of Hg in the atmosphere by a factor of two to three in the past 200 years (Driscoll et al., 2007), are mostly derived from the combustion of coal and other Hg-bearing materials (e.g., coal-fired power plants, waste incinerator facilities), and artisanal and small-scale gold mining, where Hg is used as an amalgamator (UNEP, 2013). Typically, Hg is emitted to the atmosphere as gaseous elemental Hg (Hg\textsuperscript{0}) and may stay there for a relatively long time (ca. 9 months), circulating around the hemisphere (Lindberg et al., 2007). Through various chemical processes in the atmosphere and in rain, Hg\textsuperscript{0} is oxidized to water-soluble forms (Hg(II)) that are removed from the atmosphere principally by wet deposition. Once deposited, Hg can again undergo transformation between states through various biotic and abiotic reactions, including methylation (Morel et al., 1998). Methylmercury (MeHg) is a potent neurotoxin, and can bioaccumulate in the food chain and cause detrimental effects to the health of humans and wildlife. The potential for global dispersion of Hg has resulted in a growing concern over ecosystem effects and impacts on fish consumers. Such concerns have arisen even in higher latitude northern ecosystems far removed from sources of Hg, but where elevated concentrations of Hg in fish that are consumed for subsistence have been reported (Brazeau et al., 2013). Peatlands have been found to have high MeHg concentrations and act as sources of MeHg to downstream aquatic environments (St. Louis et al., 1994; Rudd, 1995; Branfireun et al., 1996). As peatlands are the dominant landcover at higher latitudes, there is high interest in the production and transport of Hg to aquatic systems in northern Canada.

The well-documented affinity of Hg for DOM in aquatic environments (Mierle and Ingram, 1991; Ravichandran, 2004) is one that varies by both DOM quantity and quality. Changes in DOM source that occur due to hydrological variation over time are influential to the degree of Hg-DOM binding and the transport of Hg within and from a system (Hill et al., 2009; Dittman et al., 2010). Few studies have examined the temporal and spatial dynamics of Hg and DOM in high-latitude, remote peatland surface waters that discharge to the Hudson Bay and the Arctic Ocean (Kirk and St. Louis, 2009). High-frequency measurements are often burdened by logistical constraints, as implementing and maintaining field programs are high-cost endeavours in those regions. Traditional water quality monitoring programs involve the collection of discrete water samples for laboratory-based analysis. In many remote regions,
this is done at relatively infrequent intervals (weeks to months) that are insufficient to capture episodic high-flow events typically associated with the greatest exports of DOC and other solutes (Hinton et al., 1997). Thus, conventional monitoring approaches can often lead to the underestimation of solute fluxes over extended study periods, even with the use of statistical estimation techniques (Hinton et al., 1997; Cohn, 2005).

Continued improvement and advances in spectrophotometric technology has shaped it into a more flexible, rapid, and relatively inexpensive diagnostic tool in monitoring water quality on-site, and often in real-time (Hudson et al., 2007). The optically active fraction of DOM, chromophoric DOM (CDOM), is intrinsically linked with bulk DOM and its function in an ecosystem, and thus provides an accurate, alternative measure of DOM. Optical absorbance and fluorescence measurements of CDOM have been successfully employed across a wide range of ecosystems to provide high-resolution information on the dynamics of DOM source and composition (McKnight et al., 2001; Stedmon et al., 2003; Spencer et al., 2007b), and have served as an accurate proxy for DOC concentration (Spencer et al., 2007a; Downing et al., 2009; Rochelle-Newall et al., 2014), and in some surface waters, total Hg concentrations (Dittman et al., 2009; Bergamaschi et al., 2011; Bergamaschi et al., 2012).

Perhaps some of the most commonly employed and successful indices for studying the concentration and quality of DOC have been specific ultraviolet (UV) absorbance (SUVA), fluorescence index (FI), and standard DOM fluorescence (FDOM). Specific UV absorbance acts as an indicator of DOM aromaticity (Weishaar et al., 2003), the property of carbon compounds having an increased stability as a result of their molecular ring structure with alternating double and single bonds. Aromatic DOM tends to be less available for biological utilization than aliphatic DOM, which is molecularly structured as open chains. Fluorescence index provides a measure of the relative contribution of autochthonous versus allochthonous sources of DOM (McKnight et al., 2001; Cory and McKnight, 2005), since its calculation uses two reduced DOM components specific to organic matter of microbial origin and of higher-plant matter, respectively. Finally, standard FDOM (excitation 325 nm, emission 470 nm) estimates the intensity of humic-like fluorescence of DOM from terrestrial sources (Coble et al., 2014). There is also the character of hydrophobicity that is based on the polarity of organic molecules. Humic substances are generally part of the hydrophobic fraction of DOM that is preferentially adsorbed to soils and is enriched in aromatic
components, as opposed to protein-like substances that are relatively hydrophilic and bioavailable (Findlay and Sinsabaugh, 2003). Many studies support a strong correlation of SUVA or the related CDOM absorbance with DOC (Cory et al., 2007; Spencer et al., 2009), as well as with Hg (Dittman et al., 2009; Dittman et al., 2010; Burns et al., 2013) in various freshwater systems. Fluorescence index has been shown to have a strong inverse relationship with SUVA and the hydrophobic acid fraction of DOC (Balcarczyk et al., 2009; Dittman et al., 2010; O'Donnell et al., 2010). With this association, FI is presented as a good potential proxy for Hg. There is no generalizable optical measure(s) that are proxy(ies) for DOC or Hg, and the presence and/or strength of correlations vary between sites and ecosystems (e.g., Jaffé et al., 2008; Hill et al., 2009; Dittman et al., 2010; Bergamaschi et al., 2011; Rochelle-Newall et al., 2014).

Although the application of in situ sensors in the measurement of CDOM was, at first, focussed on marine and estuarine research (Coble, 1996, 2007), it is becoming a more commonly employed tool in freshwater systems (Spencer et al., 2007b; Downing et al., 2008; Saraceno et al., 2009). This has enabled high frequency, real-time monitoring in environments where traditional, campaign-based sampling may be insufficient and difficult to implement. However, in situ measurements of CDOM absorbance and fluorescence (FDOM) have not yet been applied in surface waters draining large peatland complexes, which hold an estimated one-third (270 to 450 Pg C) of the world’s soil carbon (Gorham, 1991; Turunen et al., 2002). The Hudson Bay Lowlands (HBL), the second largest peatland complex in the world, covers a vast and remote area of Canada (320,000 km²), situated in Ontario and parts of Manitoba and Quebec (Roulet et al., 1994). The region’s extensive freshwater network constitutes a major part of the Hudson- and James Bay watersheds and is a key source of freshwater and peatland-derived solutes to these aquatic environments, eventually representing 14-22% of the annual riverine input of DOC to the Arctic basin (Raymond et al., 2007; Guéguen et al., 2011). Despite its importance as a global store of carbon, predicted impacts of climate change and resource extraction on hydrology, peatland processes, and solute export, and concerns of Hg content in northern fish, the hydrology of the HBL, and its link to biogeochemical cycling in the system’s surface waters is still poorly understood (Keller et al., 2014). Warming and precipitation effects of climate change are expected to be most pronounced in high-latitude regions between 50° and 70° N, where the
majority of the world’s peatlands are found (Tarnocai, 2006; IPCC, 2007), and are likely to disrupt the delicate carbon balance of these systems. Moreover, increasing industrial activity such as mining and forestry at higher latitudes has the potential to introduce contaminants and alter hydrological systems in their surroundings.

The goal of this study was to assess the effectiveness of spectroscopic measurements of CDOM, specifically FDOM, FI, and SUVA, as high-resolution in situ proxies for DOC, THg, and MeHg concentrations in surface waters of the HBL. The objective of this investigation was to recognize physical, chemical, and environmental conditions, which may be restrictive and may cause variability in the successful application of in-stream optical measurements as proxies for the aforementioned solutes. Through this goal, there is the potential to improve the resolution and breadth of water quality data and monitoring in northern catchments, addressing the need for a better understanding of the complex hydrology and biogeochemistry of these important ecosystems. Here, the success of in situ deployments and laboratory based measurements (with potential for future in situ deployment) are evaluated for two peatland rivers of different size, structure, and stream order. Considering the association of peatlands with terrestrial humic-like DOM, it is hypothesized that in situ FDOM measurements will be highly successful as proxies for DOC and Hg concentrations in both of the study rivers found within the peatland landscape of the HBL.

3.2 Study Site

This study was conducted in the Attawapiskat River watershed in the James Bay Lowland (JBL) ecoregion, part of the HBL, approximately 500 km north-northwest of Timmins, Ontario, and 90 km west of Attawapiskat, Ontario (52.82°N, 83.88°W) (Figure 3.1). Field activities were undertaken from the De Beers Victor Diamond Mine, as this location provided accessibility to the otherwise remote peatland environment. Two sub-watersheds of different catchment size, basin geology, and stream order in the Attawapiskat watershed were investigated for this study: Nayshkootayaow River and North Granny Creek. The Nayshkootayaow River is a fourth-order river (Strahler) with a total catchment area of 1,721.8 km² that flows into the Attawapiskat River to the east of the mine (Orlova and Branfireun, 2014). The other site, the North Granny Creek, is a second-order tributary of the
Nayshkootayaow River that forms at the confluence of two first-order peatland channels with a cumulative catchment size of 30 km² (Richardson et al., 2012). Both surface water sampling points are located within the potential zone of impact of the Victor Mine pit dewatering groundwater cone of depression, resulting from pumping activities. Detailed descriptions of the Nayshkootayaow River and North Granny Creek watersheds, channels, and geology are provided in Chapter 2.2.

Figure 3.1: Map of the Attawapiskat River and tributaries in the Hudson Bay Lowlands, showing the location of the North Granny Creek (NGC) and Nayshkootayaow River (NR) sampling sites (black circles) and their respective contributing watersheds (dark and light grey), and of the De Beers Victor Mine pit (black diamond).

The study area lies within the Hudson Platform that consists of extensive flat-lying Paleozoic limestone with a dominantly calcite composition. The limestone has an average thickness of 250 m in the area, and is underlain by Archean granite-greenstone belts (Hattori and
Glacial tills were deposited by the Laurentide Ice Sheet, which covered the region and most of North America during the Quaternary glacial periods. Upon deglaciation ca. 8,000 years ago, rapid flooding led to the marine transgression of the shallow Tyrrell Sea and depositional layers of marine silts and littoral sands, generally up to 30 m thick (Glaser et al., 2004). Isostatic rebound of the formerly glaciated continent resulted in the emergence of new land from the sea, and the rapid uplift (10 mm y⁻¹) of the Hudson Bay region (FNSAP, 2010), which continues today. Poor drainage of the area, attributed to the impermeable underlying substrates, cold temperatures, and flattening of the regional topographic gradient due to postglacial uplift has promoted the establishment of coastal wetland vegetation, gradual peat accumulation, and successional evolution to a mature bog/fen landscape within the Hudson Bay physiographic region (Riley, 2011; Whittington and Price, 2012). The vast and complex mosaic of bogs, fens, and other peatland types within the HBL is the result of the accumulation of thick peat deposits, 1 to 3 m deep, over the past ca. 6,000 years (Riley, 2011).

The climate of the study region is strongly influenced by the interaction of subarctic and continental air masses, and is cooled and moistened by the presence of Hudson Bay and James Bay to the east (Riley, 2011). The area is characterized by short, warm summers, and long cold winters, with the average daily temperatures ranging from -22.3°C in January to 17.2°C in July, based on climate normals (1971-2000) from the nearest long-term meteorological site in Lansdowne House, Ontario (52.23°N, 87.88°W) (Environment Canada, 2014). On average, only 153 days of the year exhibit minimum daily temperatures above freezing (0°C). Mean annual precipitation for the region is a moderate ca. 700 mm, of which ca. 30% occurs as snowfall between October and April (Ibid.). More than 75% of rainfall over the area falls during the short, warm summer growing season, between June and September. The HBL’s climate also maintains discontinuous permafrost and permafrost features (palsas) throughout the region.

Vegetation in the bogs (nutrient-poor, domed-landforms raised above the adjacent peatland landscape) is composed dominantly of Sphagnum mosses, lichens (Cladonia spp.), and brown mosses (Amblystegiaceae spp.), often sparsely covered by an overstory of ericaceous shrubs, such as leatherleaf (Chamaedaphne calyculata) and Labrador tea (Rhododendron groenlandicum), as well as black spruce (Picea mariana). In fens (low-lying landforms, often
distinguished by alternating ridge and pool patterning, and a water table at or near the surface), vegetation is more diverse. Some of the more dominant fen vegetation indicators include sedges (Carex spp. and Scirpus spp.), sweet gale (Myrica gale), horsetails (Equisetum fluviatile), and tamarack (Larix laricina) (Glaser et al., 2004). A much denser forest of larger trees and shrubs including speckled alder (Alnus rugosa), white birch (Betula papyrifera), white and black spruce (Picea glauca and mariana), balsam fir (Abies balsamea), and balsam poplar (Populus balsamifera) are often present within the well-drained riparian areas along riverbanks (Singer and Cheng, 2002; Riley, 2011), including those of the Nayshkootayaow River.

3.3 Methods

3.3.1 Sample Collection

Water sampling was conducted over three campaigns in 2013 to focus on distinct phases of the hydrological regime: spring recession (June 5 to June 22), the summer low-flow period (July 11 to August 15), and autumn rewetting (October 16 to 25). A total of 24 and 25 surface samples were collected from each of the Nayshkootayaow River and North Granny Creek sites, respectively, for the 2013 field season at 1- to 2-day intervals during each campaign. Spring samples were collected once the Nayshkootayaow River was mostly ice-free, when substantial ice floes no longer posed a hazard. Field blanks and sample duplicates were included for every ca. 10 samples as part of an internal quality assurance and quality control (QAQC) program.

As surface water samples would be used in part for ultra-trace level mercury analysis, the “clean hands/dirty hands” sampling technique was applied as described in U. S. Environmental Protection Agency (USEPA) Method 1669 (USEPA, 1996). The method involves two samplers: “clean hands” (responsible for tasks involving direct contact with the sample), and “dirty hands” (responsible for indirect tasks), with both individuals donning clean nitrile gloves for sampling. “Dirty hands” first retrieves a double-bagged sterile 500 mL PETG sample bottle and unzips the outer bag. “Clean hands” then opens the inner bag, retrieves the bottle, rinses it three times for conditioning, and collects the sample. After inspection of the sample, “clean hands” returns the sample bottle to the inner bag and reseals it, and “dirty hands” reseals the outer bag. After collection, samples were stored in a large
clean plastic bag in ice-pack-equipped coolers for transport from the field to laboratory. Upon their return to the laboratory, samples were transferred to the refrigerator at 4 °C until filtration, within 48 hours of sample collection.

3.3.2 Sample Processing and Chemical Analysis

For each sample, a 250 mL aliquot was filtered using a PTFE vacuum filtration apparatus with acid-washed components, fitted with an acid-rinsed regenerated cellulose filter (Whatman RC55, nominal pore size 0.45 μm). Samples were filtered into clean 250 mL sterile PETG bottles, to be used for dissolved THg and MeHg analysis. From this filtered aliquot, a subsample was poured into 100 mL amber glass bottles without headspace for DOC and spectroscopic analysis. Filtered and unfiltered samples to be analyzed for Hg were acidified to 1% v/v with OmniTrace Ultra™ hydrochloric acid for preservation, freshly double-bagged, labeled, frozen, and stored in large, clean, dark-colored plastic containers at -20 °C until analysis. All other filtered samples were refrigerated and stored in the dark at 4 °C until analysis. Deionized water (DI), filter, and acidification blanks were included throughout sample processing and analyzed with samples to monitor potential contamination sources.

Samples were analyzed between 2013 sampling campaigns at the University of Western Ontario (London, Ontario, Canada). Dissolved organic carbon analyses were performed on an OI Analytical Aurora 1030W TOC analyzer using heated sodium persulfate oxidation (Method Detection Limit, MDL = 0.05 mg L⁻¹; Method Reporting Limit, MRL = 1 mg L⁻¹). Mercury samples were analyzed in the ultra-trace metals laboratory in the Biotron Institute for Experimental Climate Change Research (ISO 17025 Certified). Total mercury was analyzed on a Tekran 2600 Analyzer, using cold-vapour atomic fluorescence spectrophotometry (CVAFS) for detection, in accordance with USEPA Method 1631 (2002) (MDL = 0.03 ng L⁻¹; MRL = 0.1 ng L⁻¹). Methylmercury analyses were performed on a Tekran 2700 Analyzer according to USEPA Method 1630 (1998) (MDL = 0.005 ng L⁻¹; MRL = 0.02 ng L⁻¹). Strict QAQC procedures in accordance with the prescribed methods were maintained for all DOC and Hg analyses, including method blanks, method duplicates, matrix spikes, and secondary check standards. Any analytical runs that did not meet the required criteria were re-analyzed.
3.3.3 Optical Measurements and DOM Characterization

Spectroscopic analysis was typically done within 30 days of sample collection, with some exceptions (up to 43 days). Excitation-emission matrix (EEM) fluorescence measurements were made according to Cory and McKnight (2005) using a Cary Eclipse fluorescence spectrophotometer (Varian Inc.) equipped with a 75 Hz xenon lamp. Scans were done using the default ratio (signal: reference) mode, which minimizes the influence of lamp spectral properties. To minimize temperature effects, all samples were brought to room temperature prior to analysis. Samples were scanned in a 1.0 cm path length quartz cuvette (3.5 mL, Agilent Technologies®). Scans were collected for emission (em) wavelengths ranging from 300-550 nm at 2 nm increments over an excitation (ex) range of 240-450 nm, every 10 nm, using an integration time of 0.25 s. Slit width was set to provide a band-pass of 5 nm for both excitation and emission wavelengths. Blank EEM and Raman scans were collected daily using ultra-pure DI water (18.2 MΩ cm, Milli-Q®, Millipore®) to account for lamp decay over time (Stedmon et al., 2003). Sample EEM duplicates were run periodically to verify analytical reproducibility and instrument calibration.

Several corrections were applied to initial EEMs scans. Absorbance scans were collected on a Cary 300 UV-Vis spectrophotometer (Agilent Technologies®) from 200 to 800 nm, and were applied to fluorescence spectra following McKnight et al. (2001) to correct for inner-filter effects, the attenuation of fluorescence due to the absorption of emission and excitation light within the cuvette. Blank EEMs were subtracted from sample EEMs to remove Raman scattering McKnight et al. (2001). All sample EEMs were normalized to the area under the DI water Raman peak (Ex 350 nm), which converts EEMs to Raman units (R.U., nm⁻¹). Next, instrument-specific excitation and emission correction files, supplied by the manufacturer, were applied to each of the blank-corrected sample EEMs to account for spectral bias related to wavelength-dependent efficiencies of the instrument’s components (e.g., gratings and mirrors) and deviations in the spectral output of the light source (Stedmon and Bro, 2008). The combination of corrections and normalization allows for better comparison with other instruments.

Spectroscopic indices used to characterize sample DOM were derived from the fully corrected EEMs and were selected based on ease of application for prospective in situ use. Fluorescence index (FI) values were calculated as the ratio of emission intensities at 470 nm
and 520 nm for an excitation wavelength of 370 nm (Cory and McKnight, 2005). Fluorescence index is used to distinguish whether the source of DOM is autochthonous (microbially-derived; FI 1.7-2.0) or allochthonous (terrestrially-derived, higher plants; FI 1.3-1.4) (McKnight et al., 2001). Specific UV Absorbance (SUVA), which is strongly correlated with DOM aromaticity, was determined by dividing sample UV absorbance at 254 nm (m⁻¹) by the DOC concentration (mg C L⁻¹) (Weishaar et al., 2003; USEPA, 2009).

### 3.3.4 Hydrological Monitoring

Stage and streamflow discharge data were provided by De Beers Victor Mine for the Nayshkootayaow River, and have been reported to the Ontario Ministry of the Environment and Climate Change as part of their environmental monitoring program since 2006. Daily mean discharge measurements were calculated based on 15-minute stage data collected by submerged pressure transducers (Schlumberger Micro-Divers®, accurate to ± 0.01 m). Instantaneous discharge measurements for the Nayshkootayaow River were acquired manually on a monthly basis using a SonTek® FlowTracker® Acoustic Doppler Velocimeter, with continuous daily values calculated from stage data using a stage-discharge relationship (rating curve) from data obtained between 2008 and 2012, adjusted according to the latest six measurements, at the least. Stage readings for the North Granny Creek were also recorded using a pressure transducer, corroborated by manual readings, and were subsequently corrected for barometric pressure. Discharge for the North Granny Creek was calculated using a 15-point rating curve from the previous field season (2012). Daily precipitation data were calculated as the total of 10-minute measurements of a rain gauge located at the university research weather station, ca. 2 km northwest of the mine site.

### 3.3.5 In Situ Fluorescence Measurements

RBRmaestro sondes (RBR Ltd.), equipped with water temperature, specific conductance, pH, pressure depth, dissolved oxygen (DO), and turbidity sensors, and Turner Designs™ Cyclops-7™ fluorometers, measuring standard FDOM (ex 325±60 nm, em 470±30 nm, where ex and em wavelengths are followed by band pass values to give the full width and half width maximum), were deployed in the Nayshkootayaow and North Granny Creek and set to log at 15-minute collection intervals, with an auto-ranging gain setting. For the extended period between the second and third campaigns, collection intervals were
lengthened to 30 minutes to conserve battery life. An important assumption of *in situ* FDOM measurements is that the sensor responds only to dissolved constituents and that sediment interference from the unfiltered measurement is negligible where sediment concentrations are low (Belzile *et al*., 2006; Saraceno *et al*., 2009; Kowalczuk *et al*., 2010), such as in HBL surface waters. Raw sensor output of FDOM was converted from signal voltage (V) to units of quinine sulfate equivalents (μg QSE L⁻¹) using an 8-point calibration curve determined for each sensor. A series of concentration standards were made by dissolving quinine sulfate dihydrate in 0.05 M H₂SO₄ (Velapoldi and Mielenz, 1980; Downing *et al*., 2012).

While the logger in the North Granny Creek was deployed in the thalweg (zone of maximum velocity) of the stream, the size of the Nayshkootayaow River, limited boat access, and highly variable water levels throughout the season meant that the logger at the Nayshkootayaow River was moved to different locations along a cross-section of the river to ensure constant submersion of the probes throughout the season, while maintaining feasible access. Loggers were only briefly removed from their respective surface waters for instrument maintenance and sensor calibration at the beginning and end of each campaign. Prior to calibration, loggers were first rinsed thoroughly with tap water then with DI, and were physically cleaned with DI-moistened lint-free wipes to remove any remaining deposits.

Some of *in situ* FDOM measurements have been removed from the temporal dataset where known interruptions existed, including removal for calibration and maintenance, instrument wiring disruption, and in-stream data fouling caused by black fly larvae and periphyton sensor interference.

### 3.3.6 Proxy Correlations and Statistics

The potential of certain measurements to serve as proxies was determined based on correlative statistics between the results of laboratory chemical and spectroscopic analysis of discrete samples (DOC, THg, MeHg, FDOM, SUVA, FI), and FDOM as measured by *in situ* standard FDOM Cyclops-7 sensors. Correlations and statistical analyses were done using Prism® (GraphPad Software, Inc.).
3.4 Results

3.4.1 Hydrology and Stream Chemistry

During the study period, 173 mm of precipitation fell as rain, representing approximately 56% of the total 311 mm of rainfall in 2013. The study period was notably dryer than the climate normal, with precipitation amounting to less than 4 mm during the spring recession period (ending June 21), less than 60 mm during the summer, and to a total of 110 mm in the autumn. However, it should be noted that an additional 54 mm of rainfall fell in the month prior to the spring sampling period, which would have contributed to flow. The highest flow for the study period occurred on June 4, one day before spring sampling commenced for both the Nayshkootayaow River (58.17 m$^3$s$^{-1}$) and North Granny Creek (0.97 m$^3$s$^{-1}$) (Figure 3.2). However, annual peak flow preceded these by approximately one month (May 3 and May 8, respectively). Annual peak flows were 427.00 m$^3$s$^{-1}$ at the Nayshkootayaow River and 3.14 m$^3$s$^{-1}$ at the North Granny Creek, however stage measurements at these times were outside of the established rating curves and may be unreliable (D. Ott, De Beers Group of Companies, personal communication). Low flow occurred between June 22 and 24 (0.23 m$^3$s$^{-1}$) in the North Granny Creek, but was not reached until the end of July (July 31, 0.81 m$^3$s$^{-1}$) in the higher-order Nayshkootayaow River. Base flow conditions continued for an extended period due to low rainfall amounts and subsequent drying of the landscape during this time. Nearly half of autumn days received rainfall (total 110 mm), and of those, seven received between 5 and 25 mm of rain. Nonetheless, the greater intensity and frequency of autumn rainfall events did little to change base flow discharges in either river.

Natural flow in the Nayshkootayaow River was supplemented at a constant rate of approximately 15-20% during a portion of the 2013 sampling season using natural surface water from the Attawapiskat River. Although the flow in the Nayshkootayaow River was supplemented, water chemistry in the river continued to reflect that of large rivers in the region, while DOM and Hg relationships were representative of these waters. Moreover, seasonal changes in water quality could not be clearly attributed to the supplementation in the Nayshkootayaow.
Figure 3.2: Plots of discharge and precipitation (top), dissolved organic carbon (DOC) concentration (middle), total mercury (THg) and methylmercury (MeHg) (bottom) for the Nayshkootayaow River (left) and the North Granny Creek (right) throughout the 2013 study period. Concentrations shown are from the analysis of discrete samples collected during each of the sampling campaigns.

Dissolved organic carbon and Hg concentrations varied between sites and season (Figure 3.2). Dissolved organic carbon concentrations were higher in the North Granny Creek than in the Nayshkootayaow River throughout the study period, with DOC ranging from 15.1 to 22.8 mg L\(^{-1}\) and 10.1 to 16.5 mg L\(^{-1}\), respectively (Table 3.1). Maximum DOC concentrations were measured during the spring in the North Granny Creek and in the autumn in the Nayshkootayaow River, while the lowest concentrations occurred during the dry summer period for both rivers. The range of THg concentrations in the North Granny Creek (0.75 to 4.29 ng L\(^{-1}\)) was greater than that of the Nayshkootayaow River (0.72 to 2.87 ng L\(^{-1}\)). In both rivers, THg was highest during spring recession, decreasing gradually over the summer and into autumn. Autumn THg concentrations were similar at both sites. Methylmercury concentrations were more varied in the North Granny Creek (<MRL to 0.12 ng L\(^{-1}\)), with the
highest values observed at the same time as peak THg in the summer. In contrast, MeHg concentrations in the Nayshkootayaow River remained relatively unchanged over the study period (<MRL to 0.08 ng L\(^{-1}\)), without any clear seasonal trends.

The THg to DOC concentration ratio was highest at the start of spring measurements (June 7\(^{th}\) and 9\(^{th}\)) in both rivers, and rapidly decreased from 0.22 to 0.08 (ng of THg to mg of DOC) in the North Granny Creek and from 0.19 to 0.08 in the Nayshkootayaow by mid-July (Figure 3.3). Onwards, THg:DOC continued to decrease gradually, ultimately reaching minimum values of 0.04 and 0.05, respectively, after a period of more than three months (mid-July to late-October).
Table 3.1: Summary of mean ± standard deviation (SD), minimum and maximum values of surface water from spring, summer, and fall sampling campaigns in the Nayshkootayaow River and North Granny Creek for DOC, THg, MeHg, and optical measurements including *in situ* FDOM, SUVA, and FI. The asterisk (*) indicates outlier values.

<table>
<thead>
<tr>
<th>River and Season</th>
<th>DOC (mg L(^{-1}))</th>
<th>THg (ng L(^{-1}))</th>
<th>MeHg (ng L(^{-1}))</th>
<th>In Situ FDOM (μg QSE L(^{-1}))</th>
<th>SUVA (L mg(^{-1}) m(^{-1}))</th>
<th>FI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nayshkootayaow River</strong></td>
<td></td>
<td></td>
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<tr>
<td>Spring (freshet recession)</td>
<td>15.1 ± 0.3 (14.6-15.6)</td>
<td>2.09 ± 0.38 (1.78-2.87)</td>
<td>0.044 ± 0.020 (0.016-0.080)</td>
<td>112.8 ± 6.6 (103.4-122.1)</td>
<td>1.89 ± 0.06 (1.81-1.98)</td>
<td>1.24 ± 0.02 (1.2-1.26)</td>
</tr>
<tr>
<td>(n = 9)</td>
<td></td>
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<tr>
<td>Summer</td>
<td>12.4 ± 1.4 (10.1-14.6)</td>
<td>0.93 ± 0.20 (0.72-1.33)</td>
<td>0.042 ± 0.012 (0.019-0.056)</td>
<td>71.9 ± 13.4 (56.6-88.0)</td>
<td>1.72 ± 0.17 (1.60-1.74, 2.15*)</td>
<td>1.29 ± 0.02 (1.26-1.32)</td>
</tr>
<tr>
<td>(n = 7)</td>
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<tr>
<td>Fall</td>
<td>15.7 ± 0.5 (15.0-16.5)</td>
<td>0.89 ± 0.18 (0.72-1.10)</td>
<td>0.039 ± 0.018 (0.015-0.059)</td>
<td>130.5 ± 3.5 (125.3-134.3)</td>
<td>1.60 ± 0.09 (1.53-1.74)</td>
<td>1.31 ± 0.02 (1.29-1.33)</td>
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<tr>
<td>(n = 8)</td>
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<tr>
<td><strong>Full Study Period</strong></td>
<td><strong>14.2 ± 1.7 (10.1-16.5)</strong></td>
<td><strong>1.31 ± 0.62 (0.72-2.87)</strong></td>
<td><strong>0.042 ± 0.016 (0.015-0.080)</strong></td>
<td><strong>107.0 ± 25.3 (56.6-134.3)</strong></td>
<td><em><em>1.74 ± 0.17 (1.53-1.98, 2.15</em>)</em>*</td>
<td><strong>1.28 ± 0.03 (1.20-1.33)</strong></td>
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<tr>
<td>(n=24)</td>
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<td></td>
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<tr>
<td><strong>North Granny Creek</strong></td>
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<td></td>
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<tr>
<td>Spring (freshet recession)</td>
<td>20.7 ± 1.3 (18.9-22.8)</td>
<td>3.67 ± 0.60 (2.84-4.29)</td>
<td>0.070 ± 0.025 (0.047-0.119)</td>
<td>73.8 ± 3.1 (69.8-77.0)</td>
<td>2.10 ± 0.05 (2.03-2.16)</td>
<td>1.16 ± 0.02 (1.13-1.19)</td>
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<td>(n = 10)</td>
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<tr>
<td>Summer</td>
<td>18.7 ± 2.4 (15.1-22.0)</td>
<td>1.56 ± 0.33 (1.10-2.13)</td>
<td>0.077 ± 0.016 (0.059-0.111)</td>
<td>80.3 ± 3.7 (74.2-85.3)</td>
<td>1.85 ± 0.13 (1.71-2.13)</td>
<td>1.22 ± 0.04 (1.16-1.26)</td>
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<tr>
<td>(n = 7)</td>
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<tr>
<td>Fall</td>
<td>16.8 ± 0.5 (16.3-17.6)</td>
<td>1.01 ± 0.16 (0.75-1.23)</td>
<td>0.043 ± 0.025 (0.005-0.067)</td>
<td>78.3 ± 11.1 (63.0-92.8)</td>
<td>1.53 ± 0.09 (1.43-1.63)</td>
<td>1.24 ± 0.02 (1.21-1.26)</td>
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<tr>
<td>(n = 8)</td>
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<td></td>
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<tr>
<td><strong>Full Study Period</strong></td>
<td><strong>18.8 ± 2.2 (15.1-22.8)</strong></td>
<td><strong>2.08 ± 1.20 (0.75-4.29)</strong></td>
<td><strong>0.065 ± 0.026 (0.005-0.119)</strong></td>
<td><strong>78.1 ± 6.9 (63.0-92.8)</strong></td>
<td><strong>1.84 ± 0.25 (1.43-2.16)</strong></td>
<td><strong>1.21 ± 0.04 (1.13-1.26)</strong></td>
</tr>
<tr>
<td>(n = 25)</td>
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</tbody>
</table>
3.4.2 *In Situ* FDOM and Laboratory Analyzed Optical Measurements

During the study period, *in situ* FDOM measurements were more variable in the Nayshkootayaow River (107.0 ± 25.3 μg QSE L\(^{-1}\)) than in the smaller North Granny Creek, where they changed very little (78.1 ± 6.9 μg QSE L\(^{-1}\)), despite significant fluctuation of DOC concentrations (Figure 3.2). As with DOC concentrations, the lowest values of *in situ* FDOM for the Nayshkootayaow River were recorded in the late summer (mid-August, 56.6 μg QSE L\(^{-1}\)), while peak FDOM values were noted in the autumn (134.3 μg QSE L\(^{-1}\)) (Table 3.1). Values for laboratory measured FDOM and *in situ* logger measurements of FDOM were not significantly correlated in the Nayshkootayaow River or in the North Granny Creek (p = 0.20 and 0.94, respectively) (Figure 3.4). Changes observed in the *in situ* FDOM measurements were unlike those observed for laboratory measurements of FDOM. *In situ* measurements varied more from the mean in the Nayshkootayaow River (107.0 ± 25.3 QSE, ppb) than in the North Granny Creek (78.1 ± 6.9 QSE, ppb) (Table 3.1), while all *in situ* values varied more than their associated laboratory measured FDOM (43.8 ± 5.5 and 53.8 ± 13.3 QSE, ppb, respectively) (data not shown).

For both rivers, FI values were between 1.10 and 1.35. Similar to patterns of DOC and Hg concentrations, SUVA values deviated more from the mean in the North Granny Creek (1.84...
± 0.25 L mg⁻¹ m⁻¹) than they did in the Nayshkootayaow River (1.74 ± 0.17 L mg⁻¹ m⁻¹), where they declined gently from spring to autumn.

Figure 3.4: Measurements of fluorescent dissolved organic matter (FDOM) made by in-channel loggers (in situ) vs. by laboratory analysis on a spectrophotometer and extracted from an excitation emission matrix (EEM) for the North Granny Creek (left) and Nayshkootayaow River (right). No significant relationship was observed for either study site.

3.4.3 Correlations of Optical Measurements, DOC, THg and MeHg

Dissolved organic carbon and THg were positively correlated for both rivers (Figure 3.5), but not when the dataset was separated according to three distinct periods: spring, summer, and autumn. In the Nayshkootayaow River, there was a strong positive linear relationship between DOC and THg during the spring recession and summer ($r^2 = 0.67$, $p < 0.01$), but no relationship in the autumn. However, in the North Granny Creek, DOC and THg concentrations were positively correlated only through the summer and autumn periods ($r^2 = 0.46$, $p < 0.01$) for both filtered and unfiltered THg, while higher spring concentrations (> 2.5 ng L⁻¹) were associated with relatively constant DOC values with no significant relationship between DOC and THg.
Figure 3.5: Concentrations of dissolved organic carbon (DOC) vs. total mercury (THg) and methylmercury (MeHg) at the Nayshkootayaow River (NR; top) and the North Granny Creek (NGC; bottom) from three sampling campaigns during the study period. Linear regression lines (solid black lines) and 95% confidence intervals (dashed black lines) are also indicated. The dotted line in the MeHg plots marks the method reporting limit (MRL) of 0.02 ng L\(^{-1}\). Both datasets experience seasonal changes in relationships between THg and DOC; fall data in the NR and spring data in the NGC.

Dissolved organic carbon and MeHg were only significantly related for the North Granny Creek \((r^2 = 0.30, \ p < 0.01)\), and only for dissolved MeHg. In the Nayshkootayaow River, MeHg was not related to DOC. Likewise, MeHg was significantly related to laboratory-measured FDOM for the North Granny Creek \((r^2 = 0.48, \ p < 0.01)\), while these two parameters were uncorrelated in the Nayshkootayaow (Figure 3.6).

Dissolved organic carbon and laboratory-measured FDOM measurements were strongly correlated in the North Granny Creek and Nayshkootayaow River \((r^2 = 0.74\ and\ 0.80, \ p < 0.01, \ respectively)\) (Figure 3.6). Total Hg and laboratory-measured FDOM were also strongly correlated, however, in the Nayshkootayaow River, this was again only for spring and summer samples \((r^2 = 0.75, \ p < 0.01)\); the relationship was markedly weakened by the lack of relationship in the autumn when all data was included \((r^2 = 0.25, \ p = 0.02, \ not\)
shown). Meanwhile, the correlation between laboratory FDOM and THg in the North Granny Creek was consistent with that of DOC and THg in the stream, and was strong and positive for summer and autumn data ($r^2 = 0.71$, $p < 0.01$). However, when THg concentrations were at their highest in the spring, no relationship was observed with laboratory FDOM.

Regression analysis yielded several significant relationships between *in situ* FDOM, laboratory-derived DOM quality indices, and DOC and THg (Figure 3.7 and Table 3.2). No relationship was found between MeHg and *in situ* FDOM, SUVA or FI. For DOC and THg, stronger correlations were observed with *in situ* FDOM measurements than laboratory-based FDOM ($r^2 = 0.93$ and 0.81, $p < 0.01$, respectively). Of all the DOM quality indices and solutes measured, *in situ* FDOM measurements had the strongest and most significant correlation with DOC, which was consistent throughout all sampling periods (Figure 3.7).

Meanwhile, *in situ* FDOM and THg concentrations in the Nayshkootayaow River correlated strongly during spring and summer ($r^2 = 0.81$, $p < 0.01$), as with laboratory measurements, while the relationship was no longer statistically significant when autumn data were included ($r^2 = 0.06$, $p = 0.32$). Conversely, in the North Granny Creek, correlations did not match those presented by laboratory measurements, and relationships between *in situ* FDOM measurements and DOC, THg, and MeHg were absent.

At the North Granny Creek, SUVA and FI had relatively strong positive ($r^2 = 0.50$) and negative ($r^2 = 0.70$) relationships with DOC, respectively (Figure 3.7). In the Nayshkootayaow River, relationships similar to those in the North Granny Creek were present ($r^2 = 0.60$ and 0.65, respectively), but only when autumn data were excluded from the regression. When summer THg concentrations were not included in the North Granny Creek, relationships between SUVA and FI and THg were significant and similar in both surface waters. These relationships in the North Granny Creek resembled the one observed between laboratory-measured FDOM and THg at the same site.
Figure 3.6: Laboratory measurements of fluorescent dissolved organic matter (FDOM) vs. dissolved organic carbon (DOC), total mercury (THg), and methylmercury (MeHg) for the Nayshkootayaow River and the North Granny Creek from three sampling campaigns during the study period. Regression lines (solid black line) and 95% confidence intervals (dashed black lines) are also shown.
Figure 3.7: Correlations between in situ specific ultraviolet absorbance (SUVA), Fluorescence Index (FI), fluorescent dissolved organic matter (FDOM), and dissolved organic carbon (DOC) and total mercury (THg) for spring, summer, and fall in the Nayshkootayaow River (NR) and North Granny Creek (NGC). Solid black line and dashed grey lines represent regression lines and 95% confidence intervals, respectively.
Table 3.2: Statistics from simple regression models presented in Figure 3.7 of dissolved organic carbon (DOC) and total mercury (THg) in relation to optical measurements, including intercept, slope (β), and the respective standard errors (SE).

<table>
<thead>
<tr>
<th>Site</th>
<th>Solute</th>
<th>Parameter</th>
<th>$r^2$</th>
<th>$p$</th>
<th>Intercept</th>
<th>SE</th>
<th>β</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nayshkootayaow River</td>
<td>DOC</td>
<td>SUVA*</td>
<td>0.60</td>
<td>&lt;0.01</td>
<td>0.838</td>
<td>0.214</td>
<td>0.068</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI*</td>
<td>0.65</td>
<td>&lt;0.01</td>
<td>1.464</td>
<td>0.039</td>
<td>-0.015</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In situ FDOM</td>
<td>0.93</td>
<td>&lt;0.01</td>
<td>-81.762</td>
<td>11.961</td>
<td>13.244</td>
<td>0.832</td>
</tr>
<tr>
<td>THg</td>
<td></td>
<td>SUVA</td>
<td>0.71</td>
<td>&lt;0.01</td>
<td>1.462</td>
<td>0.041</td>
<td>0.195</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI</td>
<td>0.64</td>
<td>&lt;0.01</td>
<td>1.337</td>
<td>0.010</td>
<td>-0.044</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In situ FDOM*</td>
<td>0.81</td>
<td>&lt;0.01</td>
<td>0.072</td>
<td>0.011</td>
<td>0.044</td>
<td>0.006</td>
</tr>
<tr>
<td>North Granny Creek</td>
<td>DOC</td>
<td>SUVA</td>
<td>0.50</td>
<td>&lt;0.01</td>
<td>0.377</td>
<td>0.304</td>
<td>0.078</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI</td>
<td>0.70</td>
<td>&lt;0.01</td>
<td>1.503</td>
<td>0.041</td>
<td>-0.016</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In situ FDOM</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>THg</td>
<td></td>
<td>SUVA§</td>
<td>0.64</td>
<td>&lt;0.01</td>
<td>1.170</td>
<td>0.110</td>
<td>0.409</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
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<td>FI§</td>
<td>0.31</td>
<td>0.02</td>
<td>1.287</td>
<td>0.023</td>
<td>-0.044</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In situ FDOM</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

*The regressions used spring recession and summer data only
§ The regressions used summer and autumn data only

3.5 Discussion

3.5.1 Seasonal Variability of Streamflow, DOM and Hg Interactions

The degree of hydrological connection of peatlands to streams and rivers can affect the concentration and properties of riverine DOM from one season to the next. The metal binding affinity of DOM is also strongly tied to its structure and quality (Ravichandran, 2004; Schuster et al., 2008; Baken et al., 2011), therefore such seasonal changes to the chemical character of DOM also affect its role in the bioavailability and transport of Hg (Mierle and Ingram, 1991; Dittman et al., 2010). The temporal changes in the THg to DOC ratio observed were very similar between the Nayshkootayaow River and the North Granny Creek. At both sites, the ratio indicated that there was more THg per unit of DOC during spring recession than later on in the year. Runoff during spring snowmelt has been shown to comprise a significant portion of the annual export of Hg in upland and peatland systems (Mitchell et al., 2008; Demers et al., 2010; Haynes and Mitchell, 2012), as meltwater flowing through surface and shallow flow paths during freshet can flush stored DOM and Hg to
adjacent rivers and streams (Selvendiran et al., 2008; Dittman et al., 2010). Our THg to DOC ratios were on average slightly lower than that of 0.2 ng Hg to mg DOC reported by Grigal (2002) for the Northern Hemisphere, but were closer to this during spring recession for the Nayshkootayaow and North Granny Creek, at 0.19 and 0.22 ng THg to mg DOC, respectively. Slightly higher ratios of about 0.3 ng THg to mg DOC were reported by Dittman et al. (2010), who also suggested that these ratios could be attributed to the relationship between THg and humic hydrophobic DOM.

Previous studies have associated THg with the hydrophobic organic acid fraction of DOC, with this relationship appearing stronger than the relationship between total DOC and THg (Dittman et al., 2009; Dittman et al., 2010). The strength of this relationship is owing to more reduced sulfur sites in hydrophobic DOM that give it a greater affinity for Hg complexation (Xia et al., 1999; Haitzer et al., 2002). In our study, it is apparent that THg is indeed associated with the hydrophobic fraction of DOM, due to its strong association with SUVA, but also that this fraction does not maintain a constant proportion of the total DOC concentration throughout seasonal changes in flow conditions. Our findings differ from Dittman et al. (2010), who found that the percentage of hydrophobic organic acid in DOC and its relationship with DOC was persistent throughout the seasons. Additionally, because aromaticity is strongly associated with the hydrophobic fraction of DOM, SUVA has proven to be a strong predictor of THg concentrations (Dittman et al., 2009; Dittman et al., 2010). As in previous studies, our results revealed high aromaticity and SUVA values during spring (Spencer et al., 2009; O'Donnell et al., 2010), suggesting that the DOM contributed to streamflow during this time is hydrophobic and aromatic, with a high affinity for Hg complexation. Therefore, flow paths through the surface and shallow peat during spring and the relatively high ratios of THg to DOC at that time further suggest that THg is mobilized in association with the flushing of the aromatic fraction of DOM, to which THg binds. The correlation between DOC and THg was also notably different in autumn (Nayshkootayaow) and in spring (North Granny Creek) than during other seasons of the study period, as were some of the relationships between these solutes and their respective fluorescence and absorbance measurements. For instance, in the North Granny Creek, THg and DOC concentrations from spring samples did not appear to be correlated, for which there are various potential explanations. Likely it is speculated that the absence of a correlation was
owing to the short residence time of snowmelt in the thawing surface peat that may not have been sufficient time for Hg to bind substantially with DOM in runoff. Furthermore, the observed seasonal discontinuity in the relationships between optical measurements and DOC in both rivers did not correspond to those observed with THg.

In the case of the Nayshkootayaow River, we suggest that the changes that were observed in the autumn in DOC and THg related correlations stemmed from a relative decrease in the allochthonous aromatic hydrophobic organic acid fraction and a shift to a more hydrophilic, autochthonous source, such as deeper peat or groundwater and microbial production and alteration. Since SUVA serves as an indicator of the hydrophobic fraction of DOM to which THg binds (Dittman et al., 2009), we would expect THg to hold a constant relationship with SUVA, as was observed. Meanwhile, not all DOC is associated with the hydrophobic fraction, specifically that which is less aromatic of autochthonous origin. In the Nayshkootayaow River, the lower aromaticity (low SUVA) and increased autochthonous mixing (higher FI) in the autumn DOM corresponded to THg concentrations that did not follow the same correlations with DOC or in situ FDOM that were established in the spring and summer correlations. This suggests that THg did not bind as strongly with DOM in the autumn as it did earlier in the study period, and that autumn DOM was from a different source.

The transition away from the correlations of spring and summer corresponded to a period of periphyton growth in the late summer and autumn that was likely a source of autochthonous DOM in these otherwise relatively low-productivity subarctic waters (see Chapter 2). Because autochthonous DOM has a lower binding affinity with Hg than DOM from peatland pore waters, concentrations of THg delivered by that DOM would be much more dilute than earlier in the study period, when the peatlands and river were connected to a greater extent. This was apparent from the lower amount of THg with higher DOC concentrations in the autumn. Past studies have also proposed that DOM released directly by algae are not a source of FDOM as measured here, and are in fact mostly uncolored (Rochelle-Newall and Fisher, 2002). However, the uncolored DOM released through in situ primary production undergoes bacterial processing and alteration that results in the release of newly fluorescent DOM that is low in fulvic acid content compared to DOM from allochthonous sources (Rochelle-Newall and Fisher, 2002; Hood et al., 2005; Elliott et al., 2006; Rochelle-Newall et al.,
Thus, the increased amount of autochthonous DOM derived from primary production and its microbial alteration would have made it possible for the relationship between DOC and in situ FDOM to be maintained, while the autochthonous-like character of that DOM was unfavorable to THg binding. The changes of correlations as well as the decreasing THg to DOC concentration ratio indicates that although the measured quantity of DOM may have been similar between seasons, the DOM quality is most certainly different and does not represent the same sources or metal binding affinities.

Although THg has previously been linked with discharge (e.g., Dittman et al., 2010), DOC and THg concentrations did not reflect this in the North Granny Creek. Typically dry antecedent conditions would cause dissolved solutes to build up in the peat matrix, and be flushed by storms immediately following or ending the dry period (e.g., Bernal et al., 2006). In such a case, spikes in solute concentrations would be expected shortly following rainfall events ending the dry spell. Here, precipitation events seemed to have little effect on discharge, while both DOC and Hg concentrations appeared diluted by periods of more intense rainfall, with no observed solute peaks.

In the North Granny Creek, the lack of relationship among THg and DOC concentrations, laboratory FDOM, and SUVA in the spring suggests a break in the THg-DOC relationship with higher DOC concentrations (greater than ca. 20 mg L$^{-1}$), specifically those that occurred during this time (Figure 3.7). Recently, French et al. (2014) noted threshold-type relationships between THg binding to fulvic and humic acids and the concentration of DOC in Arctic lakes. They found that above a critical DOC concentration (11.7 mg L$^{-1}$), THg showed an increasing preference for humic acid binding sites, and less of one for fulvic acid binding sites. In turn, high DOC concentrations somewhat inhibited Hg bioavailability. Despite the similar THg to DOC ratios of the North Granny Creek and the Nayshkootayaow River throughout the study period, concentrations of both solutes were markedly higher in the North Granny Creek, which would explain why such a threshold situation was only observed here and not in the Nayshkootayaow. Given the peatland setting of the North Granny Creek and the influence of peat pore waters on DOM concentration and composition, the ability of DOM in the North Granny Creek to transport Hg would have been much different than DOM in the, at times, groundwater dominated Nayshkootayaow River (Orlova and Branfireun, 2014). Previously, Bergamaschi et al. (2011) found variability in FDOM
values at different THg concentrations in a comparison of September and April data, and suggested that these resulted from a change in DOC composition over time.

3.5.2 Proxy Potential of DOM Optical Measurements

Logger deployments, discrete sampling, and water quality monitoring throughout the 2013 ice-free season revealed the potential for in situ optical measurements to be used as effective proxies for DOC and THg in surface waters of the HBL. The strongest relationship was observed between DOC and in situ FDOM in the Nayshkootayaow River. We speculate that the absence of a relationship between in situ FDOM and DOC or THg in the North Granny Creek was the result of signal quenching at DOC concentrations above ca. 16 mg L\(^{-1}\) (i.e., an inner-filter effect). This was confirmed by a peat pore water calibration curve for the sensors that revealed a gradual and curvilinear response of FDOM intensity as DOC concentrations increased (Figure 3.8) (Watras et al., 2011). Given the strong correlations between DOC and laboratory FDOM measurements in both surface waters, it is expected that the relationship would have been almost or equally as strong in the North Granny Creek in the absence of sensor signal quenching. However, the lack of any relationship between the in situ FDOM measurements and DOC suggest that these FDOM sensors may not be useful in high DOC headwater peatland streams sustained entirely by peat-derived DOM sources. There was an evident discrepancy between laboratory and in situ measurements of FDOM (Figure 3.4). In the laboratory, FDOM was measured with a short and defined path length of light (1 cm), whereas open-faced in situ sensors, such as those used, have a longer effective path length. The sample volume and path length of such these sensors are susceptible to alteration, and may therefore be more prone to alteration or loss of the fluorescence signal in high DOC environments (Downing et al., 2012; Coble et al., 2014), especially when compared to laboratory measurements made with a short path length and controlled sample volume. However, to the benefit of researchers, in situ measurements provide the ability to capture instantaneous changes in FDOM chemistry, while such signals may be lost in laboratory measurements of FDOM due to relatively less frequent sampling intervals, and fluorescence signal degradation that may occur during sample processing or while in holding leading up to analysis. In situ measurements provided a successful proxy for DOC in the Nayshkootayaow River, owing to the abundance of terrestrially derived DOM in surface waters draining the peatland landscape and the association of FDOM measurements with the terrestrial humic-
like fluorescence region of the EEM spectra. The correlation presented suggests a high potential for use in higher order rivers of northern peatlands with groundwater contributions and similar DOC concentrations. The highly significant correlation between *in situ* FDOM and DOC concentrations in the Nayshkootayaow River ($r^2 = 0.93$) was similar or stronger than the FDOM-DOC relationship observed in previous studies covering a wide range of aquatic ecosystems (Downing *et al.*, 2009; Hill *et al.*, 2009; Saraceno *et al.*, 2009; Watras *et al.*, 2011; Rochelle-Newall *et al.*, 2014).

However, the relationships between DOC concentration and FDOM were site dependent, with seasonal variations. This was also the case for relationships involving FI, SUVA, and THg. Similar spatiotemporal variations were recently reported by Rochelle-Newall *et al.* (2014). In their study, high variability in the FDOM-DOC correlation strength, slope, and intercept was observed between sites (coastal and freshwater) and sample periods. These differences were attributed to the complexity of DOC and FDOM sources, and changes to the relative contributions of allochthonous and autochthonous carbon (Stedmon *et al.*, 2003; Rochelle-Newall *et al.*, 2014). In the Nayshkootayaow River and North Granny Creek, slight differences in the slopes and intercepts of laboratory-based FDOM-DOC relationships occurred due to a greater contribution of groundwater and primary production and thus a greater autochthonous influence in the Nayshkootayaow River, compared to the North Granny Creek.

![Figure 3.8: Plot of sensor FDOM intensity vs. DOC concentration of a peat pore water dilution series.](image-url)
In contrast, Dittman et al. (2009) found no difference in relationships between THg and UV absorbance (at 254 nm) across three study sites suggesting that the relationship was ubiquitous. In the present study, relationships between these same parameters differed slightly. However, for the North Granny Creek there was no relationship between THg and SUVA when THg concentrations were above 2.5 ng L$^{-1}$. Nayshkootayaow River THg concentrations rarely exceeded this concentration. The link between THg and the UV-absorbing aromatic fraction of DOC (Mierle and Ingram, 1991; Dittman et al., 2009) supports the change in relationships observed in the autumn for several data pairs in the Nayshkootayaow River, pointing to a loss of DOC absorbance, or input of colorless material by algal release and an associated weakening of THg binding, as noted above. It is therefore understandable that relationships observed between DOC-THg, laboratory FDOM-THg, and SUVA-THg resemble each other within a given site in our study. Meanwhile, relationship differences between sites indicate that THg does not interact with DOC in the same manner in the two surface waters.

The strength of correlations between DOC and THg, as well as between those solutes and laboratory-measured FDOM would suggest a high potential for in situ FDOM measurements to be used as proxies for DOC and THg in the North Granny Creek and Nayshkootayaow River. However, given the comparisons of DOC and FDOM with MeHg, the proxy potential of such measurements for MeHg was weak for this system. While a number of studies in other aquatic ecosystems have shown quite strong relationships between MeHg and FDOM (Hill et al., 2009; Bergamaschi et al., 2011), relationships between MeHg and DOC or DOM quality indices were non-ubiquitous, and were weak for the few exceptions where they were present in our study. Similarly, Schwesig and Matzner (2001) and Dittman et al. (2010) did not find any correlations between MeHg concentration and DOM. The variability of the MeHg-DOC interactions in different aquatic environments is highlighted in this study by the presence of relationships between MeHg and DOC and laboratory measurements of FDOM in the North Granny Creek and their absence in the Nayshkootayaow River. This lends further support to the notion that the DOM composition of source waters plays an important role in the release and transport of THg and MeHg from surface waters.

Laboratory optical measurements of fluorescence and absorbance indices varied in their effectiveness for future in-channel application. As exemplified in the Nayshkootayaow River,
**in situ** FDOM measurements enabled an augmentation of the proxy strength through instantaneous measurements, which eliminate the lag time between sample collection and processing, as well as the need for sample processing procedures that can affect DOM quality or fluorescence signal.

### 3.6 Conclusion

Dissolved organic matter fluorescence and absorbance measures have the potential to serve as proxies for DOC and THg concentrations in northern peatland surface waters. However, there is significant variability in these relationships among sites and seasons, which implies that no single optical measurements can be applied at all times, across stream orders or among watersheds. Because of the effectiveness of laboratory-measured SUVA values as a proxy for DOC and/or THg in the study rivers, it is possible that configuring in-channel loggers with both FDOM and SUVA sensors would allow for the interpretation of changes in concentration and DOM quality simultaneously, and account for the discrepancies encountered when using a single optical sensor. Additionally, to properly assess what optical measurements would be most effective for a given river size and stream order, laboratory analyses in conjunction with **in situ** measurement is strongly suggested for a statistically representative grouping of rivers of that given size within the HBL. This would ensure consistent applicability over long-term and widespread monitoring. Although the present study included a full ice-free season, a lack of substantial summer storms and of a typical autumn rewetting meant that the ability and effectiveness of **in situ** FDOM sensors to measure such events was not thoroughly tested. Such events have been shown to exhibit marked changes in DOM composition and DOC concentrations (e.g., Saraceno *et al.*, 2009; Dittman *et al.*, 2010), and could have influenced the strength of any proxy relationship found herein. While the use of optical proxies shows promise for higher-order remote northern rivers, it may be ineffective in for smaller streams with generally much higher DOM concentration. Hence, the data presented suggests that site-specific assessment over a range of flow conditions, and in more rivers of the HBL must be performed prior to entirely relying on optical proxies as a substitute for physical sample acquisition.
3.7 References


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CHAPTER 4

4 Conclusions

4.1 General Conclusions

The peatland-dominated Hudson Bay Lowlands (HBL) covers a vast area of Canada, across Manitoba, Ontario, and Quebec. Despite its importance in the global carbon cycle, impact on downstream ecosystem water quality, and concerns over its contribution of Hg to downstream communities, our understanding of hydrological and biogeochemical processes that occur internally is poor (FNSAP, 2010; Keller et al., 2014). This is not for lack of concern or interest, but largely due to logistical and operational constraints when conducting research in such an extensive and remote landscape. The purpose of the research presented in this thesis was to improve our understanding of seasonal and spatial variations in hydrological and biogeochemical connectivity between peatlands and rivers in the HBL, in Ontario, Canada. We were specifically interested in accomplishing this through the use of optical measurements of dissolved organic matter (DOM) quality that, to the best of our knowledge, have not yet been applied to characterize the HBL landscape or its fluvial networks, and have seldom been utilized in northern peatlands in general.

Another major goal of this thesis was to explore the effectiveness of an alternative to traditional low-resolution, campaign or event based grab sampling approaches by evaluating continuous in-channel measurements of fluorescence and UV absorbance as proxies for dissolved organic carbon (DOC), total mercury (THg), and methyl mercury (MeHg) in rivers of different orders within the HBL. Notwithstanding some seasonal and site-specific considerations that need to be addressed prior to being employed without physical sample corroboration, the investigated spectroscopic measurements proved to be satisfactory proxy measures for DOM and THg. Overall, we were quite successful in using standard optical measurements to elucidate seasonal and spatial changes in peat and stream water DOM quality. Notably, we observed a strong influence of in-stream primary production and microbial processing on DOM dynamics and solute interactions in rivers with a dominant groundwater input and when peatlands were relatively disconnected. A growing body of research focuses on the spatial and temporal variability of DOM quality in various aquatic environments and landscapes (e.g., Neff et al., 2006; Spencer et al., 2008; O'Donnell et al.,
2010; Mann *et al.*, 2012; Singh *et al.*, 2013), however this is the first study that documents these changes in peatland rivers of the HBL. Moreover, the effect of in-channel primary production has rarely been noted as such an important factor in controlling DOM quality and composition, particularly in a northern peatland catchment, as has been reported here.

The observed seasonal differences in DOM source in the Nayshkootayaow River indicated that the traditional calculation of a carbon mass balance (using a simple, mass flux approach) might not always be accurate when based on the concentrations measured in larger rivers draining the region. In-stream processes were shown to heavily influence the properties of riverine DOM in higher order channels at times, especially when conditions are dry and there is a diminished connection between peatlands and the drainage network. The DOC concentration in larger rivers is thus not always a reflection of the DOC exported from their peatland catchments. As an implication, calculations of peatland DOC based on transport from large rivers may result in a marked misrepresentation of the carbon stored in the system itself. Instead, a different approach to sampling may therefore be needed; one which would utilize DOM measurements from smaller (ca. first-order) streams with fewer or negligible in-channel processes, as they would offer a more representative measure of peatland-sourced DOM, and hence a more accurate calculation of the internal carbon budget of peatlands of the HBL.

As shown through spectroscopic measurements of DOM quality, runoff from surface and shallow peat layers were the prime contributor of chemistry to surface waters during spring, regardless of stream order. Perhaps with greater sample abundance for peatland pore-waters, spectroscopic results might have identified more explicit end-member sources contributing to stream water. Comparisons of the two rivers revealed changes in DOM source that differed between stream orders into the summer and autumn months, when conditions dried out, and discharge and the overall degree of hydrological connectivity decreased. For instance, the increased proportion of groundwater contribution in the Nayshkootayaow River factored into favorable conditions for primary productivity and increased microbial metabolism, which were unexpected contributors of DOM to the river and absent from the peat dominated North Granny Creek. These internal sources and processes were found to be responsible for important changes in DOM quality and interfered with the ability of *in situ* measurements of DOM to predict concentrations of DOC and THg. What this means is that extensive in-
stream primary production must be taken into account when evaluating proxy data using optical indices. Furthermore, the substantial effects of in-stream processes on optical measurements observed here emphasizes the importance of including detailed studies of internal biological processes in peatland aquatic environments and in what conditions they occur.

Results of high-resolution collection of in situ data were also of interest, showing that a continuous record of DOM quality can potentially allow us to interpret the contribution of different sources to these peatland surface waters more clearly. While it may be both logistically difficult and expensive to attain measurements of DOM and other water quality chemistry in peatland streams and rivers using traditional sampling approaches, in situ fluorescence measurements offer a means of collecting high-resolution temporal data on DOM quality and concentration, ancillary water quality chemistry, and may be telling of the degree of Hg complexation. The seasonality of DOM source was shown to have a major impact on the relationship between DOM quality (optical indices) and solute concentrations. In effect, relationships established during specific flow conditions may not be universally applied. Moreover, more frequent and extreme drying of the peatland landscape with climate change could induce more favorable conditions for in-stream primary production and be disadvantageous to implementing certain optical measurements as proxies for DOM and THg. A key implication of these findings is that, while FDOM may serve as a reliable alternative to the measurement of DOC in higher order rivers throughout varying flow conditions, caution must be observed when FDOM is applied as a proxy for THg. This would especially become the case when no other DOM quality indices (e.g., FI, SUVA) are measured, and when the presence of primary production, and promotion of microbial processing, goes unidentified. However, configuring in situ loggers with the capability of collecting optical measurements in combination, specifically in situ FDOM and either SUVA or FI, could be used as a method to overcome this issue by allowing for the interpretation of changes in DOM quantity and quality simultaneously.

Another critical contribution of our proxy assessment for optical measurements was the spatial limitation of the effectiveness of FDOM as a proxy in the peatland-dominated HBL. High DOC concentrations in small first-order (or similar) peatland streams are speculated to have caused signal quenching of in situ FDOM sensor measurements. Effectively, in situ
FDOM measurements may not be useful as a proxy tool in high-DOC headwater peatland streams, where sources of DOM are entirely peat-derived. However, the investigation of proxy potential for DOM and THg suggested that *in situ* measurements of FDOM become an increasingly powerful proxy tool for DOC and THg with increasing stream order and/or groundwater influence, such as in higher river orders of the HBL. Considering the non-universality of the spatial and temporal effectiveness of optical measurements as proxies for water quality in the HBL peatland environment, site-specific assessment of optical proxies under varying flow conditions is advised as necessary prior to substituting physical sampling for this approach. This should be investigated regardless of the aquatic ecosystem, and particularly if it is one in which the optical proxy approach has not previously been employed.

### 4.2 Recommendations for Future Work

As with many preliminary studies, incorporating greater temporal and spatial scales in future research of DOM quality and proxy measurements would be highly beneficial. Such an endeavor would help to determine if the findings presented in this thesis would persist when applied to rivers of comparable orders across the HBL watershed, and/or when studied through multi-year observations, with dominant moisture and flow conditions changing from year to year, as has proven to be the case in recent times at the De Beers Victor Mine site.

As outlined in Chapter 1, parallel factor (PARAFAC) analysis is widely used to mathematically identify and quantify underlying signals in an excitation-emission matrix that correspond to specific fractions of aquatic DOM, providing a more comprehensive picture of DOM quality than the standard optical indices used in this thesis (*e.g.*, SUVA, FI, HIX). This study involved a significant attempt to incorporate PARAFAC to provide additional, and perhaps more powerful, detail into the compositional qualities of surface and source water DOM in the study area. Unfortunately, issues that were encountered in pairing the study data with the PARAFAC code (Cory and McKnight, 2005) were unresolvable within the scope of this thesis, despite an intensive effort to correct them. Therefore, the conclusions presented here would likely be strongly reinforced through additional applications of this technique in future research of surface waters and peatlands in the HBL. Application of this analytical tool would also contribute to the current knowledge and characterization of known fluorescence
components, but would also offer the opportunity to reveal undiscovered components, perhaps unique to large northern peatland systems.

In order to properly assess the effectiveness of *in situ* FDOM measurements as a proxy for DOC and Hg, a number of modifications to the setup and testing of the in-channel instrumentation should be made. The first suggestion is based on the idea that chlorophyll is an indicator of algal biomass and can be measured continuously *in situ* alongside FDOM through sensor measurements (Coble *et al.*, 2014). The relationship between *in situ* measurements of FDOM and THg may not be stable, and can change or be lost during periods of in-channel primary production. If applied in unison with FDOM, *in situ* measurements of chlorophyll could help identify these periods of primary production and associated enhanced microbial processing, when the usefulness of FDOM as a proxy for THg may be substantially diminished. Equivalently, since different spectroscopic measurements are either more powerful proxies for DOM (*i.e.*, FDOM) or for THg (*i.e.*, FI and SUVA), configuring the *in situ* logger with additional sensors for either FI or SUVA is suggested where measurement of THg is required. To a similar extent, this study was unable to truly assess the influence of photodegradation on the in-stream DOM pool, and therefore provided a degree of speculation. This could be addressed through the installation of a sensor for photosynthetically active radiation (PAR) on the multi-channel logger. The PAR sensor would provide data on available sunlight and indication of the potential to alter DOM.

Finally, given the findings regarding the effect of concentration on FDOM sensor measurements, it is recommended that the concentration dependence of FDOM sensor accuracy be assessed in a controlled laboratory test prior to field application. This would constitute a range of DOC concentrations using diluted natural waters from the intended study site.
4.3 References


Appendices

Appendix A: Discussion of PARAFAC and related issues

This study involved a significant attempt to incorporate parallel factor analysis (PARAFAC) using the 13-component Cory and McKnight (2005) MATLAB code, in order to provide additional detail into the compositional qualities of surface and source water DOM in the study area. PARAFAC is widely used to mathematically identify and quantify underlying signals within fluorescence excitation-emission matrices (EEMs). The identified underlying signals are related to specific fractions or “components” of aquatic DOM that are used to characterize different DOM sources at a more detailed level than standard optical indices (e.g., FI, SUVA, HIX). Components are often broadly referred to as either humic-like or protein-like, depending on the unique location of their fluorescence peak in the PARAFAC-modeled excitation-emission space. Knowing which components are present in a water sample allows for deductions regarding molecular weight, oxidation state, association with biological activity, and typical source environments, among other traits. A list of commonly observed PARAFAC fluorescence components of aquatic DOM is provided by Fellman et al. (2010). Comprehensive theoretical descriptions of PARAFAC and its applications are not provided herein; instead, the reader is referred to Cory and McKnight (2005), Bro (1997), Andersen and Bro (2003) and Stedmon and Bro (2008).

Unfortunately, after reviewing the literature and consulting with a number of notable authorities on PARAFAC, we concluded that the issues encountered in pairing the study data with the PARAFAC code were unresolvable within the scope of this thesis, despite an intensive effort to correct them. Due to the technical nature of the code, not all quality assurance checks were identified and thus were not satisfied. PARAFAC analysis was therefore discarded from this thesis. The primary issues that occurred included a glitch in the raw EEM scan measurements that reoccurred at em 460 nm for every sample, regardless of the concentration, absorbance at 254 nm (A254), or sampling site. It is likely that this particular issue was derived from unresolved lamp issues with the fluorometer. Particularly, manufacturer supplied excitation-emission correction files may not have adequately corrected for the peak of xenon lamp intensity, which has been noted to occur at em 461 ± 3 nm (Cory et al., 2010). The fluorescence intensity shift at this emission wavelength was
consistently within a 10% relative difference from the preceding unaffected reading (em 458 nm), while all signals were consistently normalized to their accompanying Raman scan and corrected identically. As such, this data was found to be intercomparable for samples within this study, however vigilance is advised for inter-study comparisons.

Another key concerning issue was that the PARAFAC output yielded residual structures (i.e., peaks and troughs) rather than the acceptable noise or un-modeled variation (Murphy et al., 2013). This occurred in all samples, with the exception of blanks. Such reoccurring residual patterns indicate a poor-fit of the model, and suggest either that an inappropriate number of components may have been fit or that additional unidentified components may have been present (Lawaetz and Stedmon, 2009). Structured residuals can lead to an erroneous interpretation of the PARAFAC results. It is possible that the PARAFAC code used may not have been appropriate for the dataset (Macalady and Walton-Day, 2009), though efforts to alter the code to better fit the dataset were unfruitful. Samples had not been diluted prior to optical scans, and consequently, some $A_{254}$ values were greater than 0.3, and therefore too high for the influence of inner-filter effects (IFE) to be adequately corrected for, in some cases. The threshold value of $A_{254}$ above which inner-filter correction is no longer able to correct for IFEs varies according to individual PARAFAC components, source and quality of DOM in the samples (Miller et al., 2010). Above this threshold value, which can range from 0.3 to 0.8 (Ibid.), IFEs prevent PARAFAC from accurately identifying and quantifying given components within the sample. Correspondingly, Ohno (2002) noted that the insufficient removal of IFEs from fluorescence spectra in samples with $A_{254}$ values above 0.3 would affect the humification index (HIX), an indicator of the extent of humification introduced by Zsolnay et al. (1999). Ohno (2002) therefore presented an alternative HIX calculation that was more independent of variation in DOM concentration, and therefore more robust. Nonetheless, HIX values discussed in this thesis should be treated with discretion. As a result of the described PARAFAC issues, only those indices available from the corrected EEM are referred to in this thesis, as additional qualifiers identified through PARAFAC rely on the correct identification of calculated PARAFAC peaks and specific DOM components.
A.1 References


Appendix B: Supplementary information from principal component analyses for the Nayshkootayaow River and North Granny Creek

Figure B. 1: Bivariate mixing plot matrix for Nayshkootayaow River parameters.
Table B. 1: Eigenvalues, proportional and cumulative variances explained by principal components and rotated loadings matrix of the original variables for the Nayshkootayaow River.

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<td>δD</td>
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Figure B. 2: Scree plot of eigenvalues for derived components of the Nayshkootayaow River PCA shows that the first two components explain most of the variance in the data, using the “eigenvalue > 1” criterion and the Scree plot point of inflection.
Figure B. 3: Bivariate mixing plot matrix for North Granny Creek parameters.
Table B. 2: Eigenvalues, proportional and cumulative variances explained by principal components and rotated loadings matrix of the original variables for the North Granny Creek.

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<td>HIX</td>
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Figure B. 4: Scree plot of eigenvalues for derived components of the North Granny Creek PCA shows that the first two components explain most of the variance in the data, using the “eigenvalue > 1” criterion and the Scree plot point of inflection.
Curriculum Vitae

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