Investigating seasonal hydrology and its relationship with microbiological indicators in the Apex River watershed (Iqaluit, Nunavut)

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Abstract

Climate change in permafrost regions is projected to alter water resource distribution and water quality. The aim of this study was to characterize seasonal hydrology and dissolved organic matter (DOM) abundance and composition in the Apex River watershed in order to (1) identify water sources and pathways and (2) explore possible relationships between seasonal hydrology, DOM, and standard microbiological indicators (total coliforms (TC) and *Escherichia coli*). Discharge was measured at four sites in the Apex River (AR, CF, ET, and WT) from June 10th – August 28th, 2015. Water samples were collected three times weekly from June 8th - August 28th at the four sites and analyzed for DOC concentrations and DOM composition. Fluorescence spectroscopy and parallel factor (PARAFAC) analysis revealed the presence of five fluorescent components: three humic and two protein-like. DOM exports from the smaller east tributary (ET) exhibit predominantly protein-like (autochthonous) while DOM from the larger west tributary (WT) demonstrates humic-like (allochthonous) and protein-like (autochthonous) fluorescence. Autochthonous DOM is derived from microbial activity within water bodies while allochthonous DOM is derived from terrestrial sources. The rapid response of discharge to inputs indicates that snowmelt and precipitation runoff primarily follows overland pathways. Evidence of different timing of labile DOC availability between the Apex River outflow (AR), compared to ET, implies that controls on autochthonous DOM inputs differ between the two sites. TC densities show a correlation with protein-like fluorescence and biological freshness index (BIX). Results contribute to background knowledge which policy-makers can use to establish policies that ensure the sustainability of Iqaluit’s water resources.

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List of Common Abbreviations

AR – Apex River Site

BIX – Biological Freshness Index

CF – Confluence

CFU/mL – Colony forming units per millilitre (unit of measurement for total coliforms)

DOC – Dissolved Organic Carbon

DOM – Dissolved Organic Matter

EEM – Excitation-Emission Matrix

ET – East Tributary

FI – Fluorescence Index

HIX – Humification Index

NRI – Nunavut Research Institute

TDN – Total Dissolved Nitrogen

TOC – Shimadzu Total Organic Carbon Analyzer

PARAFAC Analysis – Parallel Factor Analysis

QSU – Quinine Sulfate Units

WT – West Tributary

Chapter One: Introduction

Climate change in permafrost regions is projected to alter water resource distribution and have detrimental effects on water quality (ACIA, 2005). Combined with increased population growth in Arctic and subarctic communities, climate change could have a significant effect on water security. In the city of Iqaluit, Nunavut, the population increased by 18.1% between 2001 and 2006. Estimated at 6,800 in 2007, Iqaluit's population is projected to grow to 13,000 by 2030 (City of Iqaluit, 2010). Such an increase will result in water resource demand which exceeds the supply provided by Lake Geraldine, Iqaluit's current water source. The City of Iqaluit has thus designated the nearby Apex[1] River watershed as a Watershed Protection Area with the intent of using it as a supplementary water supply in the future (City of Iqaluit, 2010). Before the Apex River can be formally implemented as a supplementary water supply, however, Iqaluit's General Plan requires a feasibility study which includes water quality testing, watershed mapping, identification of encroaching developments, and the identification of remedial or preventative actions to protect the water supply in the future (City of Iqaluit, 2010). Responsible management of water resources in the Apex River watershed is also recommended by Iqaluit's Sustainability Action Plan (2014).

The primary objective of this study was to develop an understanding of the sources and pathways of water in the Apex River watershed during the 2015 ice-free season through the analysis of the relationship between dissolved organic matter (DOM) and seasonal hydrology. Understanding the source of river inputs and how they could be affected by climate change is

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[1] The Apex River is sometimes referred to by it's Inuktitut name, the Niaqunguk River (City of Iqaluit, 2010). For consistency with other documents (Obradovic & Sklash, 1986; Municipal Corporation of the City of Iqaluit, 2014; Shirley, 2014), it will be referred to only as the Apex River in this document.

important for the evaluation of water resource sustainability. If the source of runoff is predominantly snowmelt, for example, decreased snow accumulation due to global warming could significantly diminish river discharge. The secondary aim of the study was to identify relationships between seasonal hydrology, DOM abundance and composition, and standard microbiological indicators (total coliforms (TC) and *Escherichia coli)* in the Apex River. Water samples were collected June 8th – October 14th, 2015, at four sites on the Apex River and analyzed for DOC, DOM fluorescence, total coliforms, and *E. coli*. Results will contribute to baseline data which city officials can use to establish policies which promote the sustainable use of Iqaluit's water resources in the future.

Chapter Two: Literature Review

2.1 Permafrost Hydrology

Arctic and subarctic hydrology differs from the hydrology of temperate regions due the presence of permafrost. Continuous permafrost is defined as ground that remains frozen for two or more years. Permafrost is overlain by an active layer, which is the layer of ground that thaws annually during the warm season. Hydrology in permafrost regions is characterized by the impermeability of deeper soil horizons which alters infiltration rates, limits subsurface water storage capacity, increases runoff ratios and concentrates hydrologic activity into a short thaw season (Woo, 2012; Kane, et al., 2008). For example, Woo (1986) shows that a reduced infiltration capacity due to the permafrost table leads to a higher runoff coefficient, defined as the amount of runoff per unit rainfall, and a more immediate river response, followed by shorter recession times. Accordingly, the depth of active layer thaw has important implications for watershed hydrology on seasonal and inter-annual basis due to its effect on infiltration rates and subsurface storage and movement.

Sources of stream water in permafrost regions include snow melt, channel precipitation, subsurface water discharge (eg. from thawing ground ice, or active layer through flow) and overland flow from rainfall-runoff events and late-season snow accumulations (Prowse, et al., 2006). Generally spring snowmelt is the largest contributor to stream discharge, however contributions from summer precipitation, subsurface water, groundwater, and melting perennial snowpacks are likely to become more pronounced as temperatures rise in response to climate change (ACIA, 2005).

Various theories of runoff generation in permafrost regions have been developed. Adopted from temperate environments, the theories of variable source area overland flow

(Dunne & Black, 1970) and partial area overland flow (Betson, 1964) have been modified to explain runoff in Arctic catchments underlain by permafrost (Carey & Woo, 2001). The variable source area overland flow describes runoff as a function of the water table depth. In uneven terrain, the depth of the water table will determine whether lower regions are saturated or unsaturated. When saturated, any precipitation that falls on these regions will escape as overland flow. Obradovic & Sklash (1986) suggest that the variable source area overland flow model may accurately reflect snowmelt conditions in permafrost environments, whereby meltwater rapidly infiltrates and saturates a thin active layer, causing subsequent overland flow. The partial area overland flow concept maintains that certain areas, such as exposed bedrock and regions of highly compacted soil or tills, remain consistent sources of overland flow as they are always highly impermeable. This concept has been adapted to explain overland runoff generated by melting accumulations of snow (Carey & Woo, 2001). Obradovic & Sklash (1986) identified partial area overland flow from major accumulations of snow as a primary contributor to streamflow in the Apex River.

Flow through the saturated subsurface zone of the active layer is also possible in continuous permafrost regions during snowmelt and throughout the thaw season (Woo, 2012). At the time of snowmelt when the active layer is still thin, subsurface flow is limited to the upper, organic layers of the soil profile (Woo, 2012; Kawahigashi, et al., 2004). However, as the thaw-season progresses and the active layer thickens, water can infiltrate into lower, mineral soil horizons. Bense, et al. (2009) developed a model of permafrost thaw which projects increased subsurface water reservoirs in response to climate warming. These subsurface water reservoirs could include storage in both saturated reservoirs (groundwater aquifers) and the unsaturated, or vadose, zone (Woo, 2012). An increase in subsurface water storage is projected to enhance groundwater discharge in Arctic and sub-Arctic permafrost regions as a result of increasing air temperature (Bense, et al., 2009). The projection of more groundwater dominated terrestrial freshwater ecosystems in permafrost regions is corroborated by Frey and McLelland (2009).

2.2 Dissolved Organic Matter (DOM) Source and Composition

DOM is a mixture of animal, plant, and microbial products smaller than 0.45 µm in diameter (Wetzel, 2001). Non-humic DOM originates from microbial sources and consists of low-molecular weight, low aromatic content (12-17%) substances such as carbohydrates, fats, proteins, and pigments (Wetzel, 2001; Miller, et al., 2009). Non-humic DOM is generally more labile, or less recalcitrant, meaning it is easily metabolized by micro-organisms, and thus turns over quickly in aquatic environments (Wetzel, 2001). Humic DOM originates from the degradation of cellulose and lignin in plant material and is therefore composed of more recalcitrant, high molecular weight compounds and a high (25-30%) aromatic carbon content (McKnight, et al., 2001).

DOM can be further characterized as allochthonous or autochthonous. Allochthonous DOM is sourced from terrestrial plant material and is transported to larger bodies of water by groundwater, soil water, or surface runoff (Wetzel, 2001). Autochthonous DOM is derived from algal biomass or microbial processes within a water body. It is generally more labile and has a lower aromaticity when compared to allochthonous DOM (McKnight, et al. 1994; Wetzel, 2001).

In permafrost environments, DOM can originate from a variety of allochthonous and autochthonous sources in a watershed which differ over the course of the ice-free season. In the early season, recalcitrant, high-molecular weight DOM is generally present near the base of snowpacks where the snow is in contact with plants and soils, but it may also be present in higher layers of the snowpack due to wind-blown deposits (Boyer, et al., 1997). Microbially-derived, non-humic DOM may also be present, in smaller quantities, if bacteria exists in the snowpack (Dubnick, et al., 2010). During snowmelt, DOM is leached from the snowpack and transported to streams by overland pathways. If snowmelt infiltrates the upper soil layers and flows through shallow subsurface pathways, it may leach additional high molecular weight, recalcitrant DOM and transport it to streams. During this period, DOC concentrations are generally higher, as sorption of C in mineral layers is prohibited by a high permafrost table (Kawahigashi, et al., 2004). As the ice free season progresses, the active layer thickens and DOM is able to percolate into deeper, mineral soil horizons where it is transformed by microbial decomposition and sorption to mineral material, producing more recalcitrant and more aromatic DOM with lower DOC concentrations (Kawahigashi, et al., 2006; O'Donnell 2010).

Since microbial activity is controlled by water temperature and light, autochthonous production of DOM is limited during the early season (Miller, et al., 2009). Hood, et al. (2003), observed increased autochthonous production of DOM in alpine lakes during the summer season when net productivity rates were highest due to longer water resident times and reduced ice-cover.

An understanding of how DOM composition varies by source provides the foundation for a conceptual model which can be used to understand sources and pathways of water. To summarize, high concentrations of DOC and highly recalcitrant, aromatic DOM are indicative of surface pathways while the existence of subsurface pathways may be indicated by recalcitrant DOM with low DOC concentrations. Finally, high concentrations of low molecular weight, low aromaticity DOM is indicative of autochthonous production from microbial sources.

2.3 DOM Characterization

Recent studies have used fluorescence spectroscopy to characterize DOM composition and understand the pre-cursor materials from which it was derived (Coble, et al. 1996; Stedmon, et al., 2003; Miller & McKnight, 2009). Coble et al. (1996), identified two main types of DOM fluorescence: humic-like which is generally associated with allochthonous sources of DOM and protein-like associated with autochthonous sources of DOM. When excited by ultraviolet radiation, certain molecules in DOM, called fluorophores, fluoresce as they return to their ground state. Fluorescence (or emission) spectra are measured across a range of excitation wavelengths, generally scanning from approximately 200 nm to 600 nm, at regular intervals (Stedmon, et al., 2003). Results of this scanning method are depicted as emission-excitation matrices (EEMs). Depending on the composition of the DOM, peaks in fluorescence intensity will be observed at difference emission-excitation wavelength combinations. Characteristic excitation/emission wavelength combinations are well summarized by Fellman, et al. (2010); combinations for select DOM compositions are described in Table 1.

Table 1 - Characteristic excitation-emission wavelength combinations for selected DOM compositions, as outlined by Fellman, et al. (2010).

Composition	Excitation (nm)	Emission (nm)	Description
UVC Humic	<260 or 320-360	448-480 or 420-460	High molecular weight, aromatic DOM most commonly found in wetlands and forested areas.
UVA Humic	290 – 325	370 – 430	High molecular weight, aromatic DOM.
Tryptophan-like	270-280	330-368	Resembles free-tryptophan, which may be indicative of lower molecular weight, less recalcitrant DOM.
Tyrosine-like	270-275	304-312	Indicative of lower molecular weight DOM and less degraded peptide material.

Indices such as the fluorescence index (FI), humification index (HIX), and biological fluorescence (or freshness) index (BIX) have also been used to understand DOM precursor material (McKnight, et al., 2001; Ohno, 2002; Huguet, et al., 2009). All indices are calculated with EEM data. Using samples from Antarctic lakes and various rivers across the United States, McKnight, et al. (2001) discovered that FI can be used as a reasonable surrogate for the aromaticity of DOM and thus can effectively differentiate between microbially (FI=1.9) and terrestrially (FI=1.4-1.5) derived DOM. FI measures the sharpness of emission peaks by returning the ratio of the emission intensity at a wavelength of 450 nm to that at 500 nm, when excited at a wavelength of 370 nm (McKnight, et al., 2001). Huguet, et al. (2009) argue that HIX and BIX are more useful indices than FI because they show a wider range of values, suggesting a higher sensitivity to changes in DOM composition due to variations in DOM source. HIX and BIX have been used in a wide range of studies to understand carbon cycling, identify DOM precursor material, and fingerprint water sources and flow paths (McKnight, et al., 2001; Huguet, et al., 2009, Williams, et al., 2010). Results of a study conducted by Huguet, et al. (2009) indicate that higher BIX values are indicative of primarily autochthonous DOM production in the Gironde Estuary, France.

Many fluorophores have overlapping or similar excitation-emission wavelengths, therefore signal processing and statistical methods are often required to quantify the existence and relative abundances of fluorophores in EEMs. Parallel factor (PARAFAC) analysis can be used to refine the results of fluorescence spectroscopy. Developed by Stedmon, et al. (2003), PARAFAC for DOM fluorescence is a multivariate modelling technique which decomposes a fluorescence signature into individual components indicative of precursor material. The relative contributions of each component can be used to understand the relative contributions of DOM sources in a given sample.

PARAFAC analysis has been used to study DOM composition in marine and freshwater samples and trace sources of DOM in diverse environments. Often, it is used to understand the composition of DOM in temperate ecosystems (Williams, et al., 2010). However, PARAFAC has also been an important tool in Arctic, Antarctic and alpine research (Cory & McKnight, 2005; Cory & McKnight, 2007; Miller & McKnight, 2010). Typically, 5-8 components are identified in a given study, however as high as 13 components have been observed (Cory & McKnight, 2005). With the exception of glacially derived DOM, studies usually detect a higher proportion of humic components relative to proteinaceous components (Dubnick, et al., 2010). The emission/excitation characteristics for the most commonly observed PARAFAC components are summarized by Fellman, et al. (2010).

2.3 DOM and Productivity in Aquatic Environments

DOM is an important driver of heterotrophic productivity in aquatic environments since heterotrophic organisms metabolize organic compounds such as DOC to produce energy. Wetzel (2001) indicates that DOM is often the primary source of energy for heterotrophic metabolism in stream and river ecosystems. Bacteria will preferentially metabolize more labile DOM produced by algae, but can utilize more recalcitrant, humic substances when algal productivity is low (Hunt, et al., 2000). Fellman, et al. (2009) found that protein-like fluorescence in temperate watersheds was a strong indicator of labile DOC that was readily taken up by heterotrophic microbes during experimental incubations. Thus, understanding the sources and resultant composition of DOM is important because it elucidates the amount of DOC readily available to support the survival of heterotrophic organisms.

2.4 Microbiological Indicators of Water Quality

Coliform bacteria are heterotrophic organisms, commonly found in aquatic environments, often used as indicators of microbiological contamination in water resources. Total coliforms (TC) comprise lactose fermenting, Gram negative bacteria such as *Enterobacter aerogenes,* *Klebsiella pneumoniae*, and the most commonly known, *Escherichia coli* (Leclerc, 2001). While not always directly harmful to humans, TC are often used as an indicator of the presence of other pathogens, such as fecal coliforms, in water sources (Environmental Protection Agency, 2016). Fecal coliforms (FC), such as *Escherichia coli* are a subset of TC which can be found in the intestines of warm-blooded animals, bodily waste, animal droppings, and naturally- occurring colonies in soils (Government of British Columbia, 2007). As heterotrophic organisms, the survival of TC and FC in soils and natural waters is enhanced by factors such as increased organic nutrient availability, solar radiation, and water temperature (Flint, 1986; McCambridge and McMeekin, 1984; Savageau, 1983). Certain coliform species are better adapted to environmental conditions than others. For example, *Escherichia coli* has a low probability of survival outside of animal intestines while species of non-fecal coliforms have demonstrated higher rates of survival in natural environments (Government of Canada, 2013; Van Donsel, et al., 1967).

There is a dearth of research and reliable data pertaining to the presence of coliform bacteria in Arctic environments. However, past research has indicated the presence of TC in water and soil samples from southwestern Alaska (Fournelle, 1967). A total coliform monitoring program was implemented by the NRI in Iqaluit in 2009. Between 2009 and 2013, TC were detected in all samples (2-2159 CFU/100mL) and low densities (<7 CFU/100mL) of *E. coli* was detected in only 10% of samples (Shirley, 2014). Total coliform and *E. coli* samples were also collected during the 2014 and 2015 ice-free seasons. This study examines 2015 data provided by NRI in an effort to understand whether the standard microbiological indicators show any relationship with seasonal hydrology or DOM abundance and composition.

Chapter 3: Methods

3.1 Site Description

This research was conducted in the Apex River watershed near Iqaluit, NU. The watershed has an area of approximately 60km^2 and is underlain by a zone of continuous permafrost (Obradovic & Sklash, 1986). Geological substrates in the watershed are dominated by till blanket (1-10m thick) and Pre-cambrian bedrock with small, localized regions of glacio-fluvial subaerial outwash plain (5-20m thick) and thin organic-rich deposits (Allard, et al., 2012). During snowmelt, water enters streamflow from the melting active layer, partial area overland flow from major snow accumulations, and interflow of snowmelt from the vegetation-bedrock interface (Obradovic & Sklash, 1986). Vegetation in the watershed is dominated by dwarf prostrate shrubs, grasses, sedges, and tundra forbs (Medeiros, et al., 2011).

The climate in the Apex River watershed is characterized as cold and dry. The 1981-2010 climate normals for daily temperature and precipitation in Iqaluit are -9.3˚C and 403.7 mm, respectively (Environment Canada, 2015). The mean summer (June – August) air temperature and total summer precipitation for 1981-2010 are 6.3 ˚C and 51.5 mm (Environment Canada, 2015). In 2015, the summer mean temperature and total precipitation were 4.0 ˚C and 60.9 mm (Environment Canada, 2015).

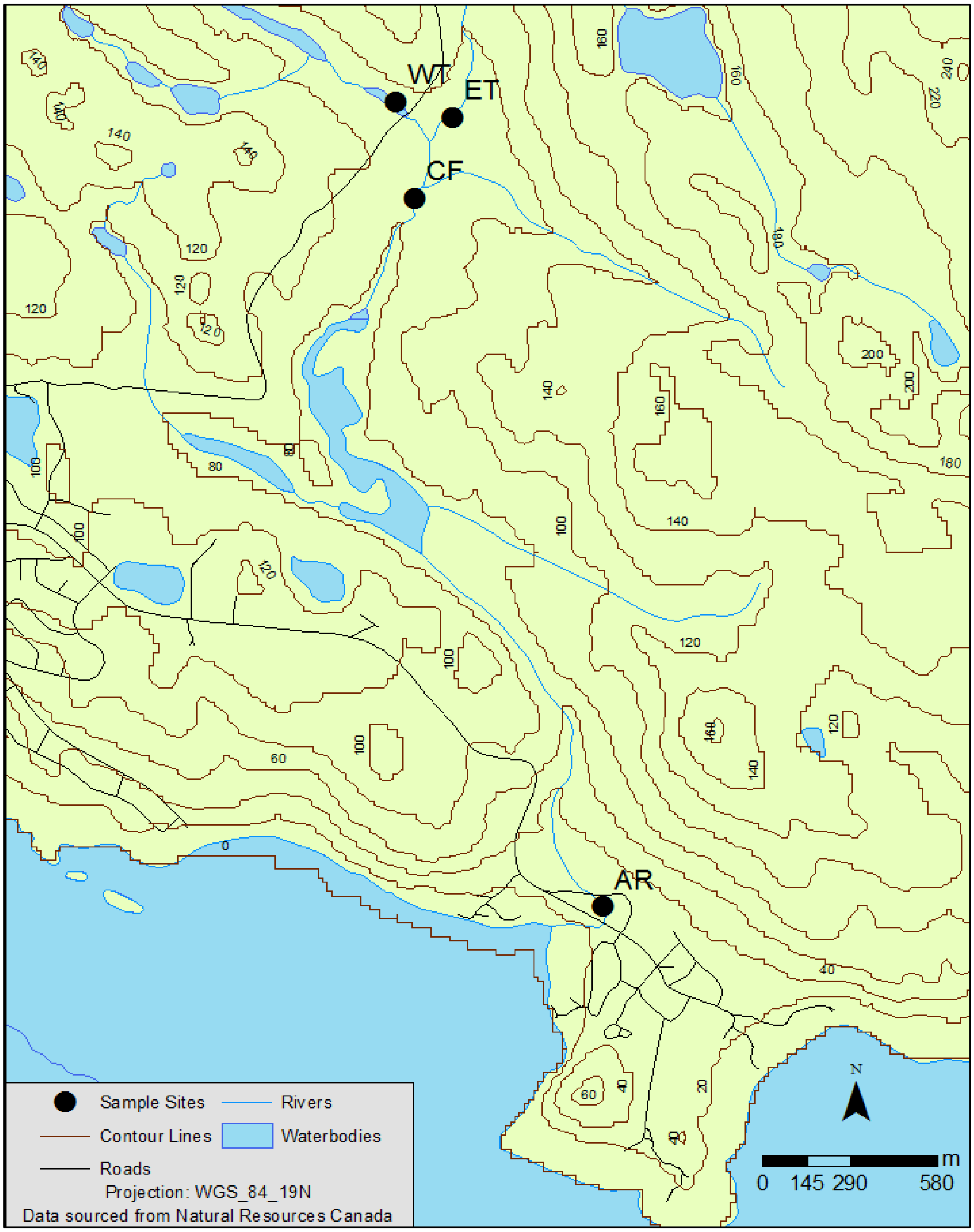

Figure 1 - Samples were collected at the east tributary (ET), west tributary (WT), confluence (CF), and Apex River outflow (AR). Map made by Bridget Rusk. Projection: UTM Zone 18T Source: Natural Resources Canada.

3.2 Field Methods

Water samples were collected from the Apex River during the 2015 runoff season by Queen's University and NRI researchers. Samples were collected at four sites (Fig. 1): the Apex River outflow (AR, 63.732˚, -68.449˚), east tributary (ET, 63.756˚, -68.459˚), west tributary (WT, 63.757˚, -68.462˚), and the confluence of the east and west tributaries (CF, 63.754˚, -68.462˚). These sites were chosen for a long-term watershed monitoring project that began in 2013. Sample collection occurred three times weekly between June 8th and August 28th. From September to October freeze-up, collection frequency was reduced to once every two weeks at the CF site only.

Samples were collected in two 500 mL Nalgene bottles that were triple-rinsed with sample water before filling. They were stored in a cooler for a maximum of one hour during transport to the Nunavut Research Institute laboratory.

Samples were filtered using a Millipore glass filtration unit and 0.47µm glass fibre filters. Filters were pre-combusted for at 450˚C for 4-6 hours to remove excess carbon. The glass filtration unit was stored in a 3% HCl acid bath to eliminate contamination from external sources of carbon. The filtration unit was rinsed with distilled water prior to use each day. It was also rinsed with distilled water and then sample water before each sample filtration. Filtered sample was separated into two certified sterile 40-mL amber EPA vials with minimal headspace and refrigerated until transport to the FaBRECC laboratory at Queen's University.

Water samples for total coliform and *E. coli* analysis were collected by NRI staff during the ice-free season. On average, samples were collected in duplicate or triplicate at the CF site twice a week along with a water temperature measurement. Samples were collected in sterilised bottles and transported to the NRI within one hour of collection. They were processed using the IDEXX Colilert Most Probable Number (MPN) method with a 24 hour incubation period (IDEXX, 2015). Results are expressed in colony forming units per millilitre (CFU/mL).

In 2015, river discharge was measured according to the area-velocity method. Current velocity (m/s, ±0.5%) was measured at 60% depth using Swoffer current velocity meter (resolution: 0.01 m/s), with a 6 s averaging interval. Discharge was measured at AR, CF, ET, and WT approximately twice weekly from June 9th to August 29th in order to capture daily fluctuations in discharge. Velocity and depth measurements were taken at verticals every 0.5 m (±0.05m) at the AR, WT, and ET sites, and every 1.0 m (±0.05m) at the CF site. For each interval, discharge (Q_i: m^3/s) was calculated by multiplying stream cross-sectional area by velocity (equation 1). The discharge at each interval was then summed to find the total discharge (Q: m^3/s) for the stream (2).

$$Q_i = depth * interval\ width * velocity \ \ (1)$$

$$Q = \sum Q_i \ \ (2)$$

Continuous stage (10 minute interval) was recorded at each of the four stream sampling sites using OnSet HOBO U20 level loggers (resolution: ±2 mm), which were corrected for barometric pressure variations using an identical logger installed on an automatic weather station in the catchment. Stage measurements were plotted against measured discharge to establish a rating curve for each stream. This rating curve was then used to derive a continuous discharge (±10%) time series at each sample site, with uncertainty calculated based on the number of verticals per cross section (Dingman, 2002). The time series for each site are not all of the same length, since icy channel conditions prohibited logger installations and discharge measurements at the ET and CF sites until later in the season. Rating curve equations are listed in Appendix A.

3.3 Analytical Methods

The fluorescence characteristics of DOM in samples were analyzed using a Horiba Scientific Aqualog benchtop fluorometer. The Aqualog emits light from a xenon lamp at a range of wavelengths to excite the molecules in a sample. As the molecules return to their ground state, they fluoresce at a specific wavelength determined by the molecular structure of the fluorescent compounds present in the sample. For each excitation wavelength, the corresponding emission wavelengths are recorded, producing an excitation-emission matrix (EEM). For this study, samples were scanned at 3 nm increments between excitation wavelengths of 240 nm and 600 nm at integration times ranging from 1-3 s. Resultant EEMs were corrected for inner-filter effects as well as for first and second order Raman and Rayleigh scattering. Fluorescence intensities were normalized to quinine sulfate units (QSU) using a 1 ppm quinine sulfate standard. The EEMs were then used to characterize the composition of DOM in the sample by identifying different fluorophores according to the emission-excitation combinations at which various components are known to fluoresce (Fellman, et al., 2010).

EEMs were also used to calculate several standard indices: the fluorescence index (FI) the biological (or freshness) index (BIX) and the humification indices (HIX) using the eemR statistical package in R (Massicotte, 2016). The FI (equation 3) was developed by McKnight et al. (2001); it is calculated by dividing the fluorescence intensity (I) at emission wavelength of 450 nm and excitation of 350nm by the fluorescence intensity at emission wavelength 500 nm and excitation wavelength 350 nm. FI indicates whether fulvic acids in DOM are microbially or terrestrially derived. The HIX (equation 4) was developed by Ohno et al. (2002); it is calculated by dividing the fluorescence intensity for the emission spectra 300-345 nm by the sum of the fluorescence intensity of the emission spectra 300-345 nm and 435-480 nm, at an excitation of 254 nm. Higher HIX values indicate more highly decomposed, recalcitrant DOM. The BIX (equation 5) was developed by Huguet et al. (2009); it is calculated at an excitation wavelength of 310 nm by dividing the fluorescence intensity emitted at emission wavelength 380 nm by the fluorescence intensity emitted at emission wavelength 450 nm. Higher BIX values (>1) are indicative of primarily fresh, labile DOM from autochthonous sources, while lower BIX values (0.6-0.7) are indicative of lower autochthonous DOM production (Huguet, 2009).

$$FI = \frac{I_{em450,ex350}}{I_{em500,ex350}} \quad (3)$$

$$HIX = \frac{I_{em300\rightarrow345,ex254}}{I_{em300\rightarrow345ex\ 254nm} + I_{em435\rightarrow480,ex254nm}} (4)$$

$$BIX = \frac{I_{em380,ex310nm}}{I_{em450,ex310nm}} (5)$$

The principal components present in the sample DOM were identified using PARAFAC analysis on 2014 and 2015 EEMs. PARAFAC analysis is a multivariate modelling technique that decomposes the fluorescence signature of a sample into its individual components and indicates the relative contribution of each component to total fluorescence (Fellman, et al., 2010). While FI, HIX, and BIX provide a more quantitative understanding of fluorescence, they are calculated based on pre-determined formulas. Since PARAFAC analysis develops models based on study-specific data, it is generally more sensitive to within-watershed variations in DOM composition (Singh, et al., 2013). PARAFAC analysis was conducted using the N-way and DOMFluor toolboxes in MATLAB and results were validated by residual and spectral sum of square error analysis, split-half analysis, and random initialization analysis, according to the tutorial published by Stedmon and Bro (2008).

DOC and TDN concentrations were analysed by high temperature combustion with a Shimadzu TOC-VPCH/TNM system. During DOC analysis (±6%), the sample was acidified to remove inorganic carbon, then combusted at 670˚C. Concentrations were calculated using a five point calibration curve (R^2>0.9999) followed by the subtraction of a Milli-Q blank (avg. = 0.057 mg/L, n=12, ±0.01 mg/L, MDL= 0.18 mg/L). Calibration details and detection limits are also summarized in Appendix B.

Ninety percent of samples were analyzed for DOC within one week of Aqualog processing in order to minimize the risk of compromised sample composition by potentially enhanced microbial activity due to vial headspace. Twenty percent of samples were duplicated within runs to calculate reproducibility and one method check ([NPOC] = 1 mg/L) was analyzed in duplicate for every five samples to determine accuracy and precision of the analytical method. If the majority of method check duplicates within a run were not reproducible within 5%, all samples would be rerun. Additionally, samples concentration was determined as average of the best three out of five (3/5) within a run. Samples were rerun if the coefficient of variation was greater than 2% and standard deviation exceeded 0.10 mg/L. Method detection limits were calculated as three times the standard deviation of NPOC concentrations in a low-concentration standard (NPOC: 0.46 ± 0.05 mg/L) plus the average NPOC concentration of the blanks, measured during each run then averaged across all runs.

Chapter 4: Results

4.1 Discharge and Precipitation

Apex River discharge during the 2015 ice-free season is characterized by an early season snowmelt response (June 8th-22nd) and subsequent rainfall-runoff responses (June 24th – July 10th) (Figure 2). Details pertaining to the rating curves used to derive the continuous discharge hydrographs are specified in Appendix A. The first discharge peaks, observed at the AR and WT gauging sites occur on June 14th -16th and correspond with snow melt. No data is available at the ET and CF gauging sites for this period, since snow and ice in the channels prevented the installation of gauging stations. Monthly precipitation in 2015 was 44% and 60% higher than the 1981 – 2010 climate normals for June and July, respectively (Environment Canada, 2015). This higher than normal precipitation translated into secondary discharge peaks observed in late June and early July due to a period of intense precipitation (June 27th – July 10th) with maximum precipitation and discharge on July 7th. Discharge recedes between July 10th and 25th and baseflow conditions are observed until August 28th. Minimal and lagged response to the July 29th

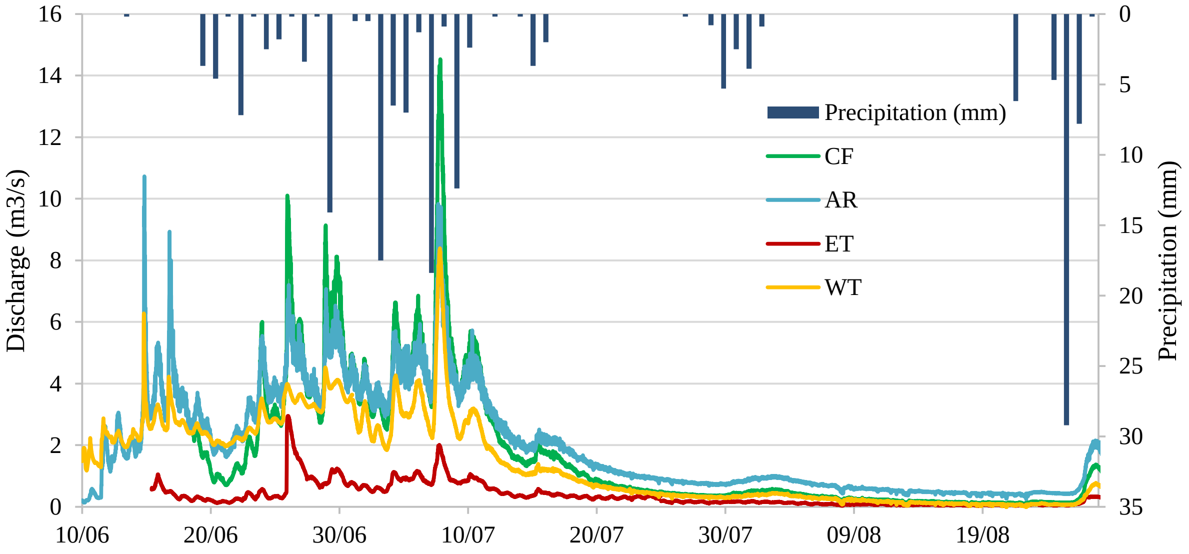

Figure 2 – Precipitation and hydrographs for the confluence (CF), Apex River outflow (AR), east tributary (ET), and west tributary (WT) gauging sites for the 2015 ice-free season between June 10th and August 28th.

– Aug. 1st precipitation event indicates a low degree of overland flow, or a high degree of infiltration and storage, likely due to low antecedent moisture conditions as well as an increasing storage capacity with active layer thickening (Woo, 1986). Response lag was measured as the difference between the start time of precipitation and the time at which discharge began increasing, following the rainfall event. The lag-to-peak period was measured as the difference between the start time of precipitation and the time of maximum discharge following the rainfall event. A rainfall event on August 26th and 27th is observed prior to the August 28th discharge peak. A comparison between the two August rainfall events shows a response lag of approximately one day for both events, based on AR discharge data. However, the first event has a lag-to-peak time of three days, while the second event has a lag-to-peak time of only two days. The shorter lag-to-peak time for the second rainfall-runoff events suggests that there was a decreased infiltration capacity in late August.

4.2. Dissolved Organic Carbon

A similar trend in DOC concentrations was observed at all sites. Maximum DOC concentrations in water samples were observed at the beginning of the ice-free season (June 8th – 12th), while minimum DOC concentrations were observed during the baseflow period. The highest concentration of the season, observed at ET on June 8th, was 5.14 mg/L. Mean DOC concentration across all sites during the snowmelt period (June 8th – June 14th) was 2.87 mg/L (Standard Deviation (SD) = 028 mg/L) . Smaller peaks in DOC concentrations were observed on June 22nd and July 8th due to rainfall-runoff events. Mean DOC concentration across all sites during the high rainfall-runoff period from June 24th – July 14th was 1.85 mg/L (SD = 0.12 mg/L). A final peak in DOC concentrations on August 28th corresponds with the observed rainfall-runoff event during the same period. During the baseflow period, mean DOC concentration across all sites drops to 1.25 mg/L (SD=0.09 mg/L). AR consistently has the highest DOC concentrations relative to the other three sites, however the difference in site means was not significant (F=0.69, p>0.05).

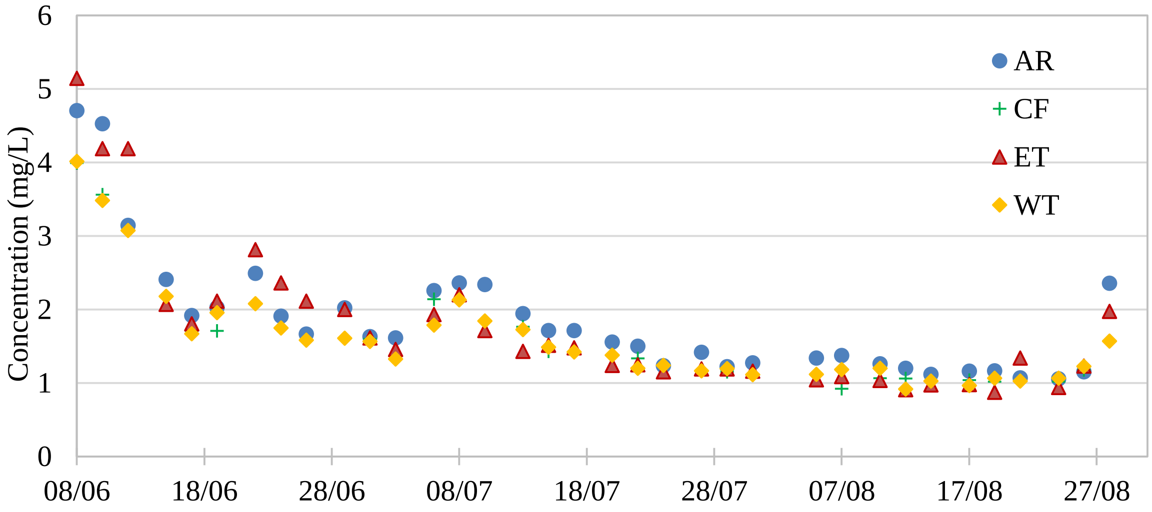

Figure 3 - Dissolved organic carbon concentrations from samples collected three times weekly at the Apex River outflow (AR), confluence (CF), east tributary (ET), and west tributary (WT) sites during the 2015 ice-free season between June 8th and August 28th. Error bars (±6%) are not shown in this diagram because they do not exceed the size of the symbols.

4.3 Fluorescence Indices

FI, BIX, and HIX were calculated for each sample site. There were no significant trends in FI at any of the sites. BIX (Figure 3) at ET showed the most variation (SD=0.369) while BIX at WT showed the least variation (SD=0.146). Linear regression demonstrates significant increasing trends in BIX over time at ET (F=4.99, $0.01<p<0.05$), CF (F=18.07, $P<0.01$), and WT (F=10.25, $P<0.01$). There is also an increasing trend over time observed at AR, however it is not statistically significant (F=3.36, $p>0.05$). An increasing trend in BIX at all sites as the ice-free season progressed indicates increasing DOM lability. Higher BIX values at the ET site in late July and early to mid-August, with the highest BIX values on August 5th and August 12th, indicate that DOM inputs at ET were predominantly autochthonous compared to other sample sites. HIX values show an inverse relationship to BIX. A decreasing trend in HIX at all sites, although statistically insignificant ($p>0.05$), could indicate reductions in DOM recalcitrance, and thus higher DOC lability overall, as the season progressed. The inverse relationship between HIX and BIX is further exemplified by the occurrence of minimum HIX at ET on August 5th and August 12th. The highest HIX value of the season occurs at AR on August 21st.

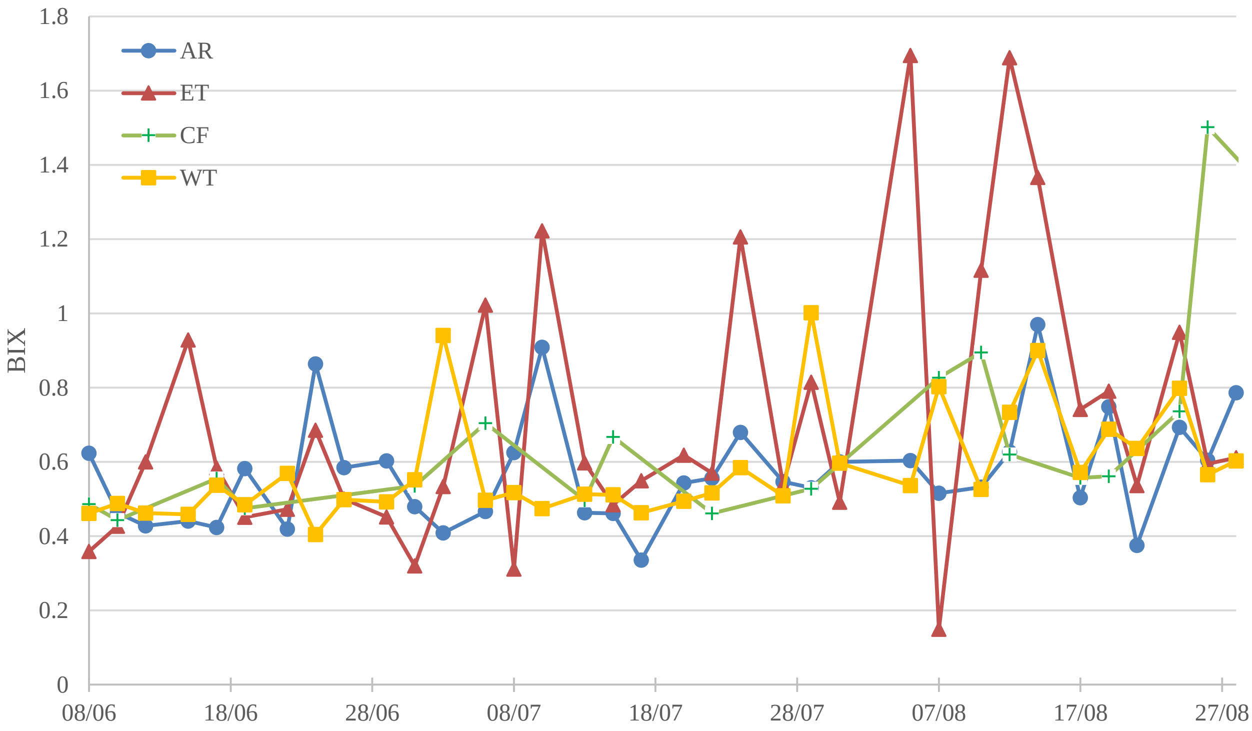

Figure 4 - Calculated freshness index (BIX) values for the 2015 ice-free season at the Apex River outflow (AR), east tributary (ET), confluence (CF), and west tributary (WT). BIX generally increases as the ice-free season progresses, with strong fluctuations observed at the ET site during the baseflow period.

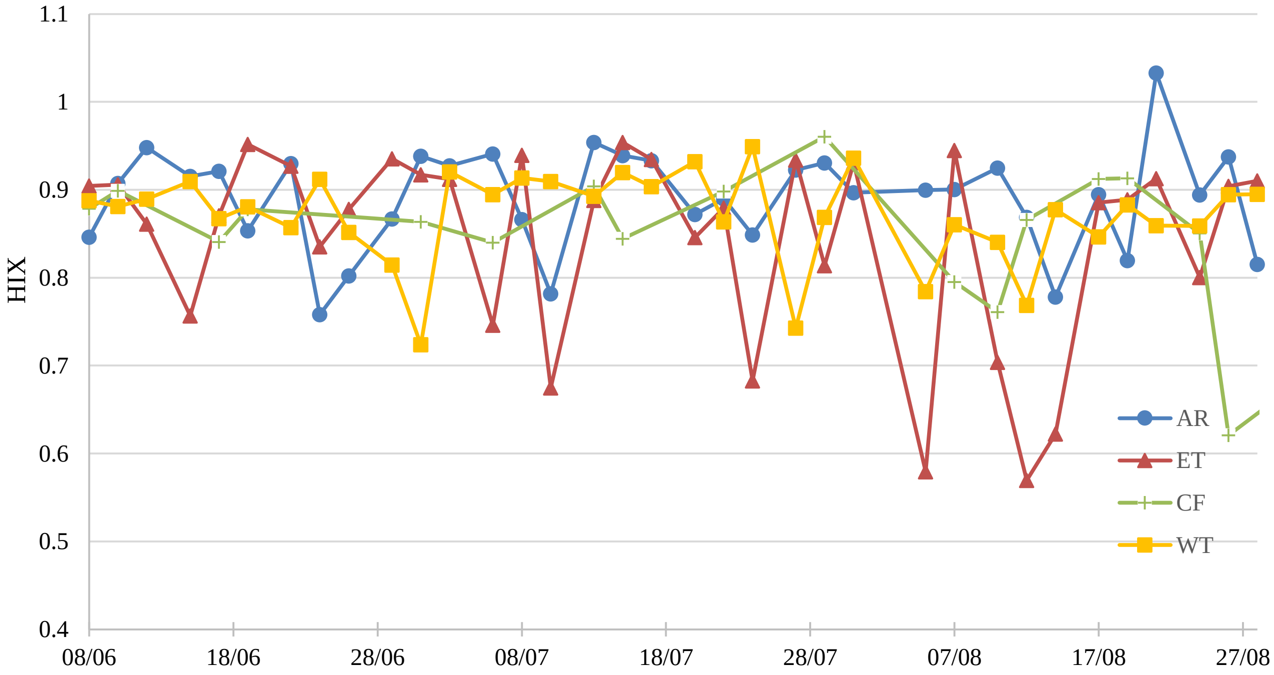

Figure 5 - Calculated humification index (HIX) values for the AR, ET, CF, and WT sites from June 8th to August 28th, 2015. The HIX indicates the degree of humification of DOM and should have an inverse relationship to BIX. Results show that the recalcitrance of DOM in ET samples varies the most throughout the ice-free season.

4.4 PARAFAC Analysis

According to the validation requirements outlined by Stedmon & Bro (2008), it was determined that the data (n=271) was best described by a five-component model. The five components: UVC humic, UVA humic, humic-like, tryptophan-like, and protein-like (Table 1 and Figure 5) were identified using the criteria provided by Fellman, et al. (2010). The UVC humic peak is indicative of high molecular weight, aromatic DOM characteristic of allochthonous origin in forested or wetland regions. The UVA humic peak is also indicative of high molecular weight, aromatic DOM of allochthonous origin. The third, humic-like component has been observed in other studies (Cory & McKnight, 2005), however a closer examination of sample EEMs does not support its existence in the Apex River dataset therefore it will not be further discussed. The fourth (tryptophan-like) and fifth (protein-like) components are characteristic of low molecular weight, less recalcitrant, autochthonous DOM (Fellman, et al., 2010).

The UVC humic (Figure 7), UVA humic, and protein-like components follow similar trends at all sample sites. However, the contribution of the tryptophan-like component varies markedly between sites over the course of the season (Figure 8). Most notably, peaks in tryptophan-like fluorescence are observed at AR during each of the season’s major discharge events. At ET, contributions from tryptophan-like fluorescence are highest during the rainfall-runoff event in early July and during baseflow. Peaks in tryptophan-like fluorescence at WT occur on July 1 and August 27. The highest contribution from tryptophan-like fluorescence at CF is observed on August 24.

Fluorescence index results and PARAFAC results were compared in order to understand whether there was relationship between the indices and fluorescence components observed in

Apex samples. At all sample sites, correlation analysis indicates weak correlations between HIX and both the UVA and UVC humic component (|r|<0.28). At the ET and CF sites, there are stronger negative correlations between the intensity of the tryptophan-like component and HIX (ET: r=-0.85, CF: r =-0.69). Strong positive correlations are also observed between the intensity of the tryptophan-like component and BIX at the ET (r = 0.80) and CF (r = 0.69) sites. At WT, a negative correlation was observed between BIX and tryptophan-like fluorescence intensity (r=-0.15) as well as between HIX and tryptophan-like fluorescence intensity (r=-0.75). Finally, a negative correlation between the tryptophan peak intensity and HIX (r = -0.30) and a positive correlation between tryptophan and BIX (r=0.18) were observed at AR. Overall, the strongest correlations were observed between the tryptophan-like fluorescent component and both HIX and BIX at the both the CF and ET sites.

Table 2 – The PARAFAC model components, as outlined in Fellman, et al. (2010), identified for the Apex River using 2014 and 2015 data (n=271). The UVA and UVC humic components are indicative of DOM from terrestrial sources while the tryptophan-like and protein-like components are commonly attributed to autochthonous DOM production. The humic-like peak was invalidated following individual EEM analysis, and thus will not be further discussed.

Component	Excitation (nm)	Emission (nm)	Description
UVC Humic	260	448-480	High molecular weight, aromatic DOM most commonly found in wetlands and forested areas.
UVA Humic	250-295 or 360-385	478 - 504	High molecular weight, aromatic DOM.
Tryptophan-like	240 or 270-280	330-368	Resembles free-tryptophan, which may be indicative of lower molecular weight, less recalcitrant DOM. Indicative of autochthonous DOM.
Humic-like	250	550	More reduced DOM, often correlated with the ketone/aldehyde carbon. (Cory & McKnight, 2005)
Protein-like	240 or 300	338	Indicative of amino acids, free or bound in proteins. Strongly resembles free-tryptophan. Characteristic of autochthonous DOM.

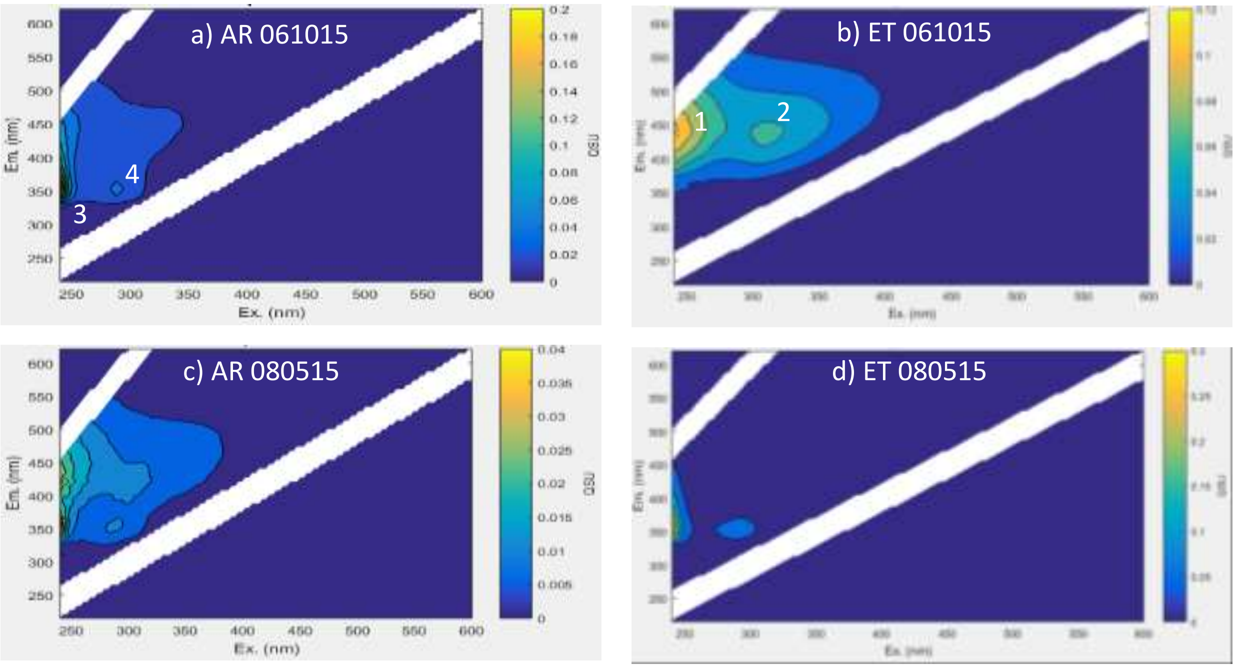

Figure 6 – Selected EEMs from 2015 Apex River samples demonstrate spatial differences in the contribution of autochthonous DOM between the snowmelt period, depicted by AR 061015 (a) and ET 061015 (b), and the baseflow period, depicted by AR 080515 (c) and ET 080515 (d). Numbered peaks are (1) UVC-humic, (2) UVA-humic, (3) tryptophan-like, and (4) protein-like. Stronger contributions from tryptophan- and protein-like components are observed at AR during snowmelt (a) and at ET during baseflow (d).

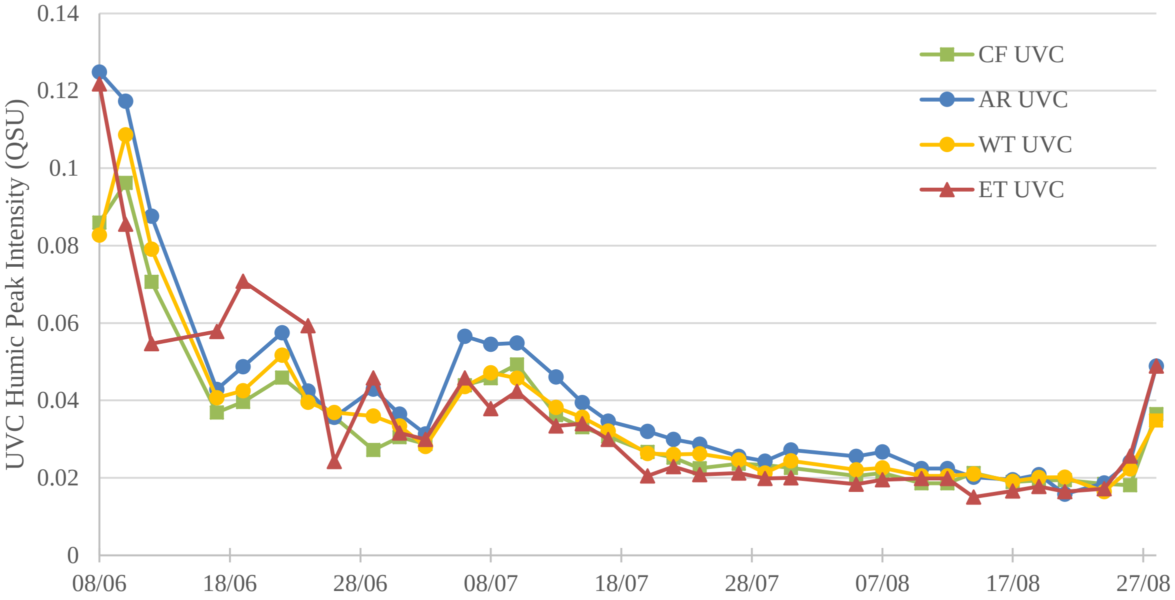

Figure 7 - Intensity of the UVC humic peak (in QSU) at the AR, CF, ET, and WT sites between June 8th and August 28th, 2015. The UVA humic and protein-like components follow a similar trend.

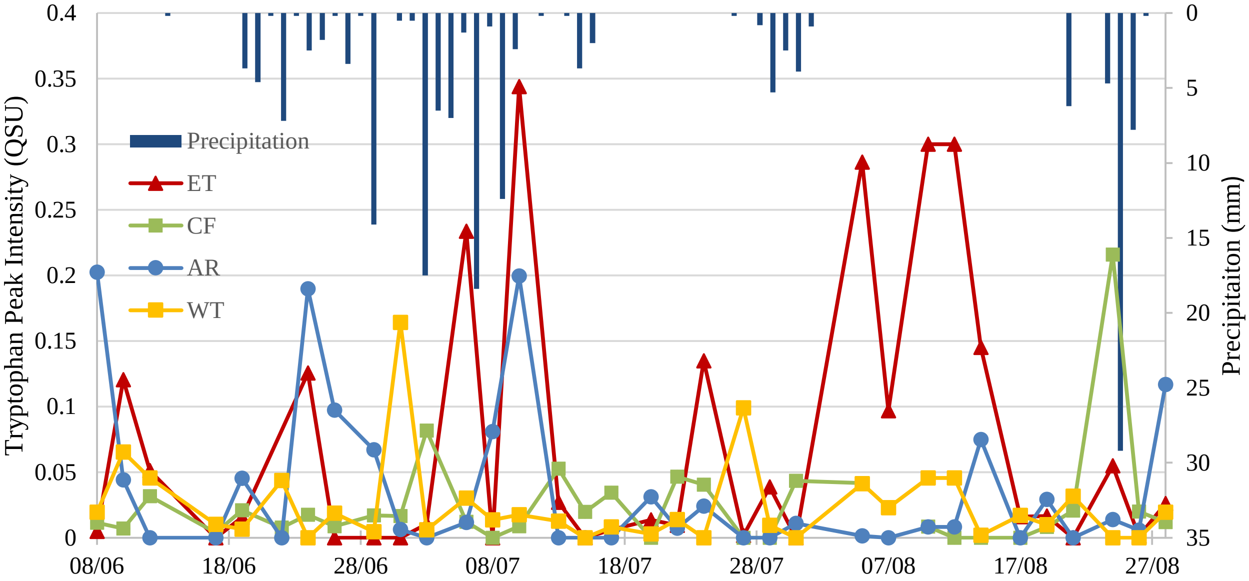

Figure 8 - Intensity of the tryptophan-like peak (in QSU) at the Apex River outflow (AR), confluence (CF), east tributary (ET), and west tributary (WT) sites during between June 8th and August 28th, 2015. Results show that the contribution of the tryptophan fluorescence varies the most throughout the ice-free season with the strongest variations in the ET samples. Peaks in tryptophan fluorescence at AR correspond with major discharge events related to snowmelt and subsequent summer precipitation events.

4.5 Microbiological Indicators

Total coliforms (TC) and *E.coli* prevalence is minimal in the Apex River during the 2015 ice-free season. TC was detected in all samples (n=61) at low densities ranging from 3.1-113 CFU/mL (standard error = 9.66 CFU/mL). For comparison samples collected from Lake Winnipeg, located in a more temperate environment with anthropogenic influences, had a TC MPN ranging from 1-1600 CFU/mL (Pip & Allegro, 2010). In general, TC densities in the Apex River were higher during the late season baseflow period (Figure 7). However, localized TC maxima also occur during major precipitation events on July 6th and August 26th. Limited correlation analysis was possible due to the poor temporal resolution of coliform data; only 18 samples for coliform analysis were collected concurrently with samples for DOC and DOM analysis. Of all the water quality indicators measured (water temperature, fluorescence components, BIX, HIX, and DOC) the strongest relationship existed between TC densities and BIX (n=18, r=0.50). A similar correlation was observed between TC densities and the intensity of the tryptophan peak (r=0.46).

E. coli (Appendix D) was detected in only 8.2% of samples at low levels ranging from 1.0-5.2 CFU/mL. Due to the low prevalence, *E. coli* densities did not have any observable correlation with seasonal hydrology and thus will not be further discussed.

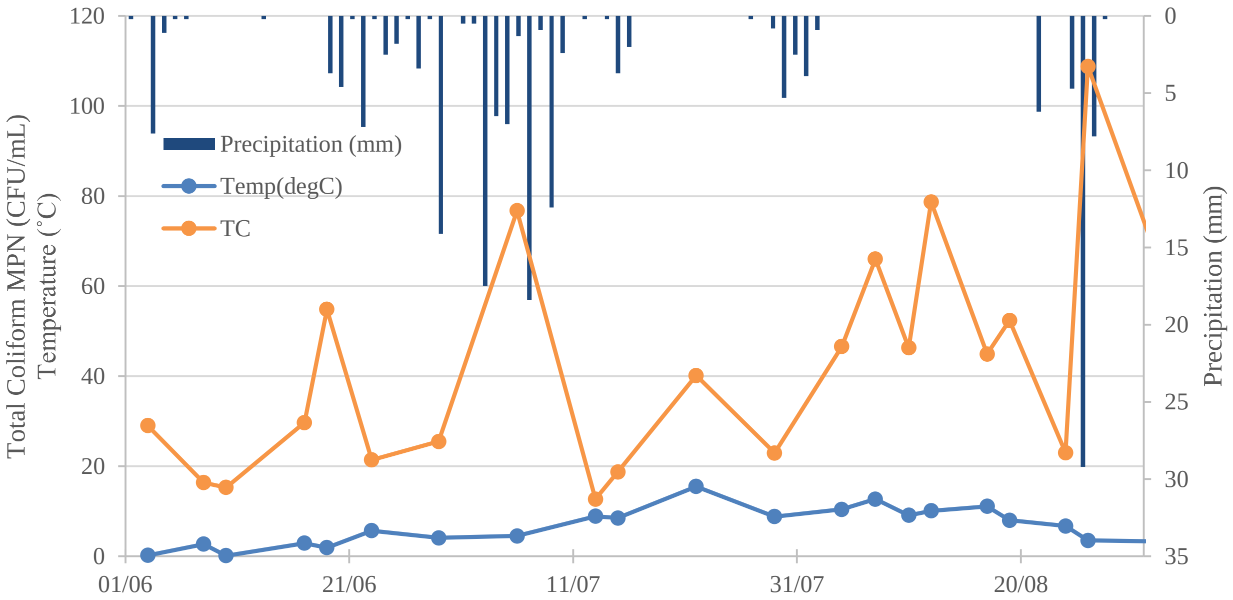

Figure 9 – Total coliform (TC) counts and water temperature of samples collected at the confluence (CF) twice weekly between June 3rd and August 26th, plotted with precipitation.

Chapter 5: Discussion

The main objectives of this study were to characterize sources and pathways of water in the Apex River watershed during the 2015 ice-free season and investigate the existence of a relationship between seasonal hydrology, DOM abundance and composition, and the prevalence of standard microbiological indicators (TC and *E. coli*). Considering the data obtained from hydrograph analysis, DOC quantification, and fluorescence spectroscopy, this study provides insight into the influence of snowmelt and summer precipitation on seasonal discharge as well as DOM inputs and sources of water specific to each sample site. Furthermore, results elucidate a relationship between TC densities and hydrological conditions that could be used as the basis for future water quality research in the Apex River.

5.1 Sources and Pathways of Watershed Inputs

5.1.1 Influence of snowmelt and summer precipitation on seasonal discharge

Hydrograph analysis for the four gauging sites (AR, CF, ET, and WT) provides preliminary insight into the seasonal variations in sources of water in the Apex River watershed during the 2015 ice-free season. The Apex River exhibits seasonal flow variations typical of subarctic continuous permafrost regions (Rouse, et al., 1997), with contributions from both snowmelt and summer precipitation that are similar in scale. However, the complete snowmelt peak was not captured in our discharge measurements thus it cannot be confidently concluded that the contribution from snow melt is a low as depicted. Furthermore, while climate change studies predict increased summer precipitation in Arctic regions, it is currently difficult to identify trends in climate at Iqaluit due to poor records which do not differentiate between snow and rainfall (ACIA, 2005; Kjikjerkovska, 2016). Detailed precipitation data, which differentiates between snow and rainfall, as well as contributions to discharge from precipitation should be more closely monitored in the future in order to ensure that high contributions from summer precipitation events are not abnormal and falsely relied upon for the sustainability of the Apex River as a water resource.

5.1.2 Snowmelt and rainfall-runoff pathways

At all samples sites, DOC concentrations exhibit relationships to discharge which are consistent with past studies in alpine and permafrost environments (Spence, et al, 2015). Analyzed alongside fluorescence data, DOC concentrations can be used to determine the flow paths that convey water to the Apex River. Humic-rich DOM and high DOC concentrations indicate overland or shallow subsurface pathways while humic-rich DOM with low DOC concentrations generally results from water that has infiltrated into the active layer and flowed through deeper subsurface pathways in mineral soil horizons (Hood, et al., 2003; O'Donnell, et al. 2010). Autochthonous DOM is characterized by a reduced humic component and low DOC concentrations (McKnight, et al., 1994; McKnight, et al., 1997).

The elevated DOC concentrations and humic-rich DOM observed during the snowmelt period and early season rainfall-runoff events suggest that water primarily follows overland or shallow subsurface pathways. It is expected that the DOM leached from surface soils during overland or shallow subsurface flow would be rich in humic substances, such as cellulose, lignin, and plant-derived components, and fairly recalcitrant, since organic matter in soils is subject to enhanced microbial decomposition (White, et al., 2008). Indeed, at all sites, BIX values are lowest during the snowmelt period and early season rainfall-runoff events, indicating the presence of more highly decomposed DOM. Additionally, PARAFAC results reveal increased contributions from UVA and UVC humic components.

DOC concentrations and DOM compositions observed in water samples collected during the two baseflow period precipitation events (July 29 – August 1 and August 26-27) demonstrate that runoff pathways differed between the two events. Changes in stream DOC concentration and DOM composition are not observed during the July 29 – August 1 precipitation event. Hydrograph analysis indicates that there was a limited and lagged discharge response to this precipitation, suggesting increased infiltration and storage in soils during the event. An increased storage capacity due to low antecedent moisture conditions and a thickening active layer would limit runoff via overland flow and thus reduce DOM inputs into the Apex River. During the late August precipitation event, however, an increase in DOC concentrations and humic-like fluorescence is observed at all sample sites. Similar to the early season runoff events, high DOC concentrations and increased humic-like fluorescence indicate that runoff from the August 26-27 precipitation event followed overland or shallow subsurface pathways to the Apex River. Increased runoff by overland pathways suggests reduced infiltration in late August. Decreased infiltration of precipitation may be due to the intensity of the event, which was higher than the precipitation event in early August or due to higher antecedent moisture conditions from the rainfall event earlier in August. Due to poor data records, projected changes in precipitation in permafrost regions are uncertain, however the majority of studies indicate that increases in precipitation are expected (ACIA, 2005). Consequently, understanding how the intensity of precipitation events and a thickening active layer affect runoff and the subsequent introduction of DOM into aquatic ecosystems will be an important objective for further research.

5.1.4 Site-specific variations in water sources

Hydrographs and DOM abundance and composition also allow for the identification of water sources, and their relative contributions to downstream discharge, at specific sample sites.

Most notably, lower discharge at the ET site throughout the ice-free season demonstrates that it makes a smaller contribution to streamflow relative to WT and suggests that the ET drains a smaller portion of the watershed than the WT. This is consistent with results from a 2013 study in the Apex River which attributed 86% of discharge to the WT and 14% of discharge to the ET, based on stable isotope analysis (Kjikjerkovska, 2016).

HIX and BIX values and PARAFAC analysis reveal that DOM in ET may be dominated by autochthonous sources during baseflow, while WT receives DOM input from a variety of lakes, surface runoff pathways, and streams throughout its catchment. Predominantly higher BIX and lower HIX values at ET during the baseflow period are indicative of less recalcitrant, autochthonous DOM derived from microbial activity. These values are supported by an increasing contribution of tryptophan-like fluorescence observed in PARAFAC results during the same period. A large lake in the southeastern corner of the Apex watershed may be the source of this autochthonous production (Kjikjerkovska, 2016; Miller & McKnight, 2010). The large increase in BIX values in the absence of snowmelt and rainfall-runoff inputs suggests this lake is likely a major contributor to streamflow at ET.

HIX and BIX values at the WT site are consistently more subdued than at the ET site, indicating a proportionally smaller autochthonous contribution to DOM in the west catchment. The absence of dominating tryptophan-like fluorescence in WT samples from the baseflow period is further evidence of a proportionally smaller contribution from autochthonous production. These results imply that the WT is fed by a variety lakes, surface runoff pathways, and streams throughout its catchment. Further study of the distribution and water balance of inputs to the west catchment is required in order to understand the sustainability of current WT water sources and thus the WT’s contribution to downstream discharge.

PARAFAC results from the CF site indicate DOM of predominantly UVC and UVA humic composition throughout the ice-free season, with decreasing DOC concentrations as the season progresses. The results imply that DOM at the CF is primarily allochthonous throughout the season with water input pathways moving from overland and shallow subsurface flow to deeper subsurface flow as the season progresses. Since discharge at WT is higher than at ET, we would expect DOM composition at CF to more closely resemble DOM observed at WT. Indeed, HIX and BIX values are more subdued at CF, compared to ET, as they are at WT. Furthermore, trends in the relative contributions of tryptophan-like and humic-like fluorescence are similar at CF and WT. The high contributions of tryptophan-like fluorescence observed at ET during the baseflow season are not reflected downstream at the CF site. This is likely due to the proportionally smaller contribution of ET to downstream discharge combined with the decomposition of labile DOM introduced at ET as it travels downstream to the confluence (Stedmon & Markager, 2005).

Similar to the patterns observed at CF, strong contributions from UVA and UVC humic components paired with decreasing DOC concentrations at the AR site indicate a predominance of allochthonous DOM with water pathways moving from overland flow to deeper subsurface flow as the season progresses. Interestingly however, peaks in tryptophan-like fluorescence and BIX values are observed at the AR during snowmelt and rainfall-runoff events. Similar results have been observed in Alaskan watersheds and are considered characteristic of wetland dominated streams (Fellman, et al., 2009). The phenomenon was not consistently observed at the other sample sites. Areas of pooling water observed between the CF and AR sites may behave like wetlands, driving increased autochthonous production of lower molecular weight DOM. These areas are also a center for summer recreational activities such as swimming, bathing, and dog walking which could introduce proteinaceous organic matter or disturb sediments. During snowmelt and rainfall-runoff events, increased discharge between the CF and AR sites could flush proteinaceous, low-molecular weight DOM from these pools downstream, resulting in the observed peaks in tryptophan-like fluorescence and BIX.

5.2 Microbial Indicators

TC density maxima are observed during intense rainfall-runoff events, suggesting that overland flow washed bacteria from terrestrial sources into the Apex River at the CF site. Terrestrial soil environments are more favourable for coliform bacteria survival and past studies have observed similar spikes in water TC densities due to stormflow (Van Donsel, et al., 1967). There are also more peaks in TC density observed throughout the baseflow period despite a reduction in the DOC available for metabolism. This suggests that coliform bacteria survive in the river despite lower runoff inputs and are likely not C limited. This could be possible if DOM in the stream is more labile and thus more readily available for uptake by heterotrophic organisms, or if C is not the limiting nutrient (Fellman, et al, 2009). An increase in NO_3^- concentrations observed at the same site may indicate that survival is due to an enhanced availability of N in more labile DOM (M. Lafrenière, personal comm., March 23, 2016). A rise in BIX and increased contributions from the tryptophan-like component at the CF site as the season progresses do indicate that DOM is autochthonous and thus likely more labile, with a lower C:N ratio (McKnight, et al. 1994). Alternatively, enhanced coliform survival due to higher water temperatures during the baseflow season could produce the higher TC densities observed (Van Donsel, et al., 1967). However, no significant correlation between TC densities and water temperature was observed at the CF site during the 2015 ice-free season.

While TC is not an ideal indicator of waterborne pathogens, since not all coliforms are pathogenic, the presence of TC can be an indicator of water source susceptibility to contamination (Health Canada, 2015). Fecal coliforms are a subset of total coliforms, and thus could respond to environmental conditions, such as increased nutrient concentrations, in a similar manner to the observed TC response in the Apex River. If this is the case, the results of this study indicate that baseflow in the Apex River produces conditions favourable to fecal coliform bacteria survival and presents an increased risk of microbial contamination in the water source.

It is important to note the short-term temporal variation in TC densities observed in the Apex River. TC densities can vary by as much as 85.8 CFU/mL between consecutive samples. This is characteristic of coliform bacteria, which can vary diurnally (Traister & Anisfeld, 2006). DOM composition can also change over the period of only a couple of days, due to flushing during snowmelt and rainfall-runoff events. It is thus important to understand how coliform bacteria densities respond to these events, which could potentially provide more nutrients for heterotrophic metabolism. The short-term variations in TC densities and DOM composition observed in the Apex River provide a rationale for more frequent sampling of TC and *E. coli*.

There is a weak positive correlation between BIX and TC densities as well as between tryptophan-like fluorescence and TC densities. Since increased BIX and tryptophan-like fluorescence are indicative of autochthonous inputs of DOM, this could indicate that TC densities have relationship with autochthonous DOM. For example, autochthonous DOM could provide nutrients for heterotrophic metabolism, as previously discussed. Alternatively, it is possible TC itself fluoresces, produce the observed increases in tryptophan-like fluorescence and BIX. Further research is required to understand the relationship between TC densities, BIX, and tryptophan-like fluorescence.

Regardless of the relationship, the unique temporal patterns of tryptophan-like fluorescence and increased BIX at the AR site indicate the need for enhanced monitoring near the outflow of the Apex River into Koojesse Inlet. Currently, samples for TC and *E. coli* analysis are only collected at the CF site. However the results of this study indicate that DOM composition at the CF and AR sites may vary independently, particularly during snowmelt and rainfall-runoff events. Therefore, it is possible that TC densities also vary independently between CF and AR. In order to adequately capture both temporal and spatial variations in coliform bacteria densities, samples for TC and *E. coli* analysis should be collected at both the AR and CF sites.

5.3 Study Limitations

The use of DOC as an indicator of water source is subject to error, especially when impacted by climate change. Seasonal changes in DOC concentrations observed in this study are typical of rivers in both Arctic and temperate regions, where DOC concentrations increase with increased discharge (Lewis & Grant, 1979; Striegl et al, 2005). However, under the influence of climate change, increased active layer depth due to rising temperatures could lead to longer residence times of DOC in soils, allowing for enhanced microbial decomposition of DOC and decreased release of DOC with overland flow (Streigl, et al., 2005; O'Donnell, et al, 2012). Alternatively, increasing temperatures could result in increased DOC export to streams in permafrost regions where abundant organic matter, or peat, is present at depth (Frey & Smith, 2005). The uncertainty regarding DOC fluxes under the influence of climate change could confound efforts to use DOC concentration as an indicator of water sources and pathways. Because of this uncertainty, it will be important to study other indicators, such as stable isotopes and ions, in order to identify water sources and pathways in permafrost environments affected by climate change.

A second major limitation of this study is the spatial and temporal resolution of coliform data. In 2015, coliform data was only collected at the CF site. Thus, sample analysis provided information about water quality at that specific point in the river. Spatial variations in hydrology and water quality observed at the four sites in this study highlight the need to monitor microbial indicators in more than one location, since conditions governing the survival of bacteria vary from site to site. Furthermore, coliform data was only collected 1-2 times weekly and 18% of samples were not collected at the same time as stream samples collected for the analysis of DOM and other water quality indicators (temperature, suspended sediment, pH, and electrical conductivity). Since coliforms often vary diurnally, improved temporal resolution of coliform data would provide better understanding of densities in the Apex River throughout the season. Additionally, coordinating fieldwork such that all samples are collected at the same time, would facilitate the investigation of relationships between coliform densities and other water quality indicators.

5.4 Policy Implications and Further Research

This study responds to calls for responsible management of the Apex River watershed and the implementation of studies to assess the river's feasibility as a municipal water source for the City of Iqaluit (City of Iqaluit, 2010; Municipal Corporation of Iqaluit, 2014). The findings of this study indicate that future research commissioned by the city should focus on (1) understanding how precipitation trends will be affected by a changing climate, (2) understanding mechanisms that control water sources in the WT catchment, and (3) enhanced temporal and spatial resolution of monitoring for standard microbial indicators.

Opportunities for further research also lie in the concurrent study of additional hydrological indicators such as stable isotopes of hydrogen (δD) and oxygen ($\delta^{18}O$), and major anions (Cl^-, NO^{2-} , NO_3^-, Br^-, SO_4^{2-}, PO_4^{3-}) and cations (Na^+ , NH_4^+, K^+ , Mg^{2+} , Ca^{2+}, Sr^{2+}). NO_3^- anion data combined with total dissolved nitrogen (TDN) analysis would allow for the calculation of C:N ratios which provide further insight into DOM composition and source (Wetzel, 2001). Stable isotopes of hydrogen and oxygen, can act as tracers of water age and source in order to perform hydrograph separation as observed in the studies performed by Obradovic & Sklash (1986) and Kjikjerkovska (2016). Combined with DOC concentrations, DOM fluorescence, and ion data, stable isotopes would allow for a much more detailed picture of water sources and pathways in the Apex River throughout the ice-free season. Finally, as the Apex River monitoring project continues and baseline data accumulates, analysis of inter-annual variations in water sources and pathways, as well as water quality, will be essential in order to understand how these watershed characteristics change over the long-term.

6.0 Summary

(1) Under the mutually reinforcing pressures of climate change and a high population growth rate, the City of Iqaluit has designated the Apex River watershed as a Watershed Protection Area with the intent of using it as a supplementary water supply in the future.

(2) The main objectives of this study were to (1) develop a better understanding of the sources and pathways of water in the Apex River watershed during the 2015 ice-free season and (2) determine if there was a relationship between seasonal hydrology, DOM abundance and composition, and microbiological indicators of water quality.

(3) Hydrograph analysis indicates that Apex River discharge is highest during snowmelt and early summer rainfall-runoff events. Lower discharge at ET indicates that the east tributary drains a smaller portion of the watershed than the west tributary, thus contributing less to downstream discharge.

(4) Elevated DOC concentrations and strong contributions from UVA and UVC humic components observed at all sites during snowmelt and early season precipitation events suggests that the majority of runoff follows overland or shallow subsurface pathways.

(5) Stronger variations in BIX and tryptophan-like fluorescence at ET indicate that DOM inputs are primarily autochthonous, while more subdued BIX and tryptophan-like fluorescence at WT indicate that DOM is derived from a variety of allochthonous and autochthonous sources.

(6) Decreasing DOC concentrations and predominantly humic-like DOM indicated by PARAFAC analysis fluorescence indices at the CF imply that DOM at the CF is primarily allochthonous throughout the season with pathways moving from overland flow to deeper subsurface flow as the season progresses.

(7) Peaks in BIX and tryptophan-like fluorescence during the snowmelt and rainfall-runoff events were uniquely observed at AR suggesting that DOM inputs at the site are controlled by wetland conditions or recreational activities (bathing, washing, dog walking, etc.) which occur downstream of the CF, WT, and ET sample sites.

(8) TC densities increase during the baseflow period, but also exhibit localized maxima during the two rainfall-runoff events of the season (early July and late August). TC densities are correlated with BIX and tryptophan-like fluorescence, indicating that increased autochthonous inputs of labile DOM containing N could enhance the survival of coliform bacteria in the Apex River.

(9) No pattern of *E.* prevalence was observed during the 2015 ice-free season and no correlation could be established between *E. coli* prevalence and other measured parameters including temperature, DOC, DOM composition, rainfall or discharge.

(10) Further research in the Apex River should include an investigation of precipitation trends, more detailed analysis of water sources in the west catchment, enhanced monitoring of standard microbiological indicators such as TC and *E. coli*, and studies of inter-annual variation in water sources and water quality in the watershed.

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Appendix A – Rating Curves Used for the Derivation of Continuous Discharge

Table 3 - Rating curve equations used for the calculation of continuous discharge at the AR, CF, ET, and WT sites. The rating curves were based on n cross sections of velocity measurements conducted throughout the season at varying times of day in order to capture diurnal fluctuations in discharge. Discharge at ET was calculated using two equations to reflect that the gauging site was changed on July 25th. Discharge at WT was calculated using two rating curves because the morphology of the river was altered by a bank flooding event during the early season.

Site	Dates Applicable (2015)	Rating Curve Equation	R^2	Number of Cross Sections (n)	Uncertainty*
AR	06/10 – 08/29	$y = 8.18x^{3.57}$	0.719	n=13	±10%
CF	06/18 – 08/29	$y = 53.27x^{5.72}$	0.973	n=10	±10%
ET 1	06/15 – 07/25	$y =14.80x^{2.81}$	0.649	n=5	±10%
ET 2	07/25 – 08/29	$y =20.95x^{3.57}$	0.950	n=6	±10%
WT 1	06/10 – 06/30	$y = 4.70x - 0.59$	0.824	n=6	±10%
WT 2	06/30– 08/29	$y = 16.68x^2 - 14.67x + 3.20$	0.995	n=9	±10%

*All uncertainties were between 7-8% and rounded to 10% due to irregularities in channel morphology at all sites.

Appendix B - Dissolved Organic Carbon Analysis

Table 4 - Descriptive statistics for the analysis of non-purgeable organic carbon (NPOC) used to obtain DOC concentrations at the AR, CF, ET, and WT sites.

Site	n	Average (mg/L)	Maximum (mg/L)	Minimum (mg/L)	Standard Deviation (mg/L)
AR	35	1.854	4.707	1.059	0.855
CF	39	1.627	3.995	0.882	0.708
ET	35	1.764	5.144	0.875	0.986
WT	35	1.610	4.015	0.920	0.697
Overall	144	1.710	5.144	0.875	0.0798

Table 5 - System and calibration parameters for the Shimadzu TOC-VPCH/TNM used to analyze DOC concentrations in 2015 Apex River samples.

System and Calibration Parameters	Description
Detector	Combustion
Catalyst	TC/TN High Sensitivity
ASI Tray	40 mL Vials
Injection Volume	150 µL
NPOC Injection Settings (best of)	3/5
Calibration Curve	Five-point (R^2>0.9999)
Sample Reproducibility (n=35)	6%
Method Detection Limit	0.160 mg/L
Mean Blank Concentration (n=12)	0.567 mg/L
Mean Method Check Concentration (n=11)	1.027 mg/L

	Site DOC (mg/L)			
Date	**AR**	**WT**	**ET**	**CF**
08/06/2015	4.707	4.015	5.144	3.995
10/06/2015	4.527	3.484	4.190	3.563
12/06/2015	3.144	3.075	4.190	2.874
15/06/2015	2.410	2.179	2.069	2.392
17/06/2015	1.918	1.671	1.807	1.712
19/06/2015	2.026	1.959	2.115	1.712
22/06/2015	2.494	2.078	2.813	2.221
24/06/2015	1.909	1.750	2.362	1.667
26/06/2015	1.665	1.583	2.115	1.540
29/06/2015	2.023	1.609	2.000	1.677
01/07/2015	1.633	1.565	1.613	1.601
03/07/2015	1.613	1.329	1.459	1.540
06/07/2015	2.257	1.786	1.933	2.139
08/07/2015	2.362	2.130	2.201	2.100
10/07/2015	2.340	1.843	1.714	2.055
13/07/2015	1.946	1.726	1.431	1.766
15/07/2015	1.715	1.488	1.514	1.433
17/07/2015	1.712	1.421	1.479	1.576
20/07/2015	1.559	1.379	1.240	1.299
22/07/2015	1.502	1.202	1.247	1.336
24/07/2015	1.234	1.241	1.155	1.247
27/07/2015	1.421	1.165	1.191	1.239
29/07/2015	1.222	1.198	1.194	1.155
31/07/2015	1.274	1.114	1.162	1.162
05/08/2015	1.342	1.118	1.045	1.097
07/08/2015	1.376	1.184	1.088	0.924
10/08/2015	1.261	1.202	1.035	1.065
12/08/2015	1.203	0.920	0.908	1.063
14/08/2015	1.120	1.027	0.973	1.061
17/08/2015	1.160	0.968	0.979	1.041
19/08/2015	1.165	1.066	0.875	1.020
21/08/2015	1.069	1.029	1.342	0.924
24/08/2015	1.059	1.064	0.941	1.018
26/08/2015	1.151	1.228	1.231	1.177
28/08/2015	2.359	1.572	1.973	1.561
15/09/2015				0.952
25/09/2015				0.992
09/10/2015				0.997
14/10/2015				0.882

Table 6 - Results of DOC analysis at AR, WT, ET, and CF.

Appendix D – PARAFAC Model Component Loadings

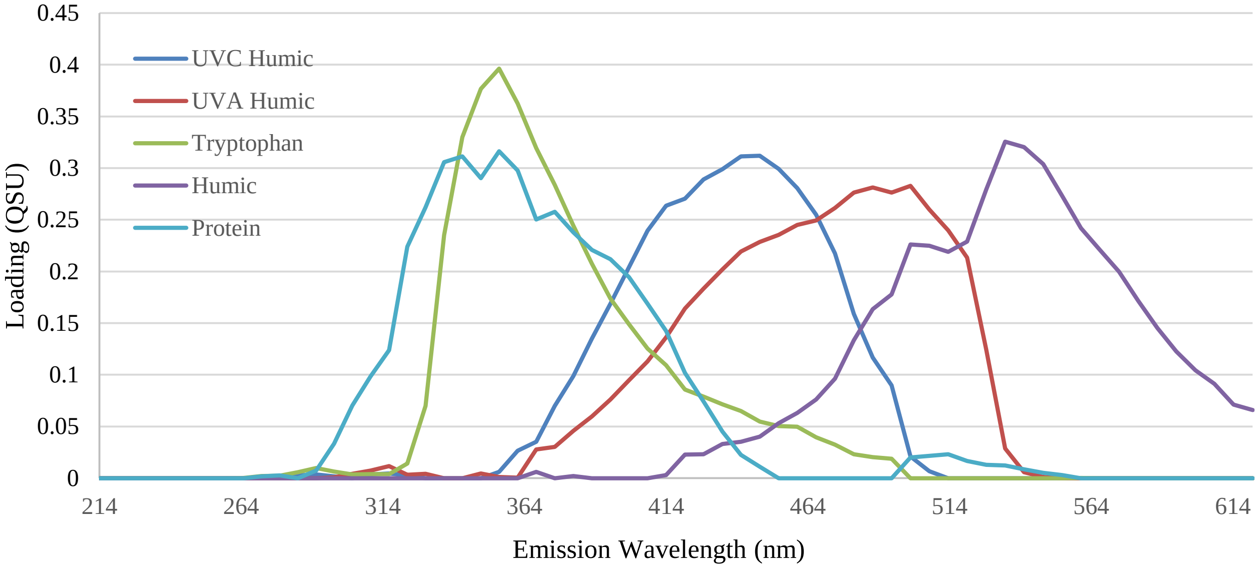

Figure 10 - Emissions loadings (in QSU) for the five-component PARAFAC model derived from 2014 and 2015 Apex River samples.

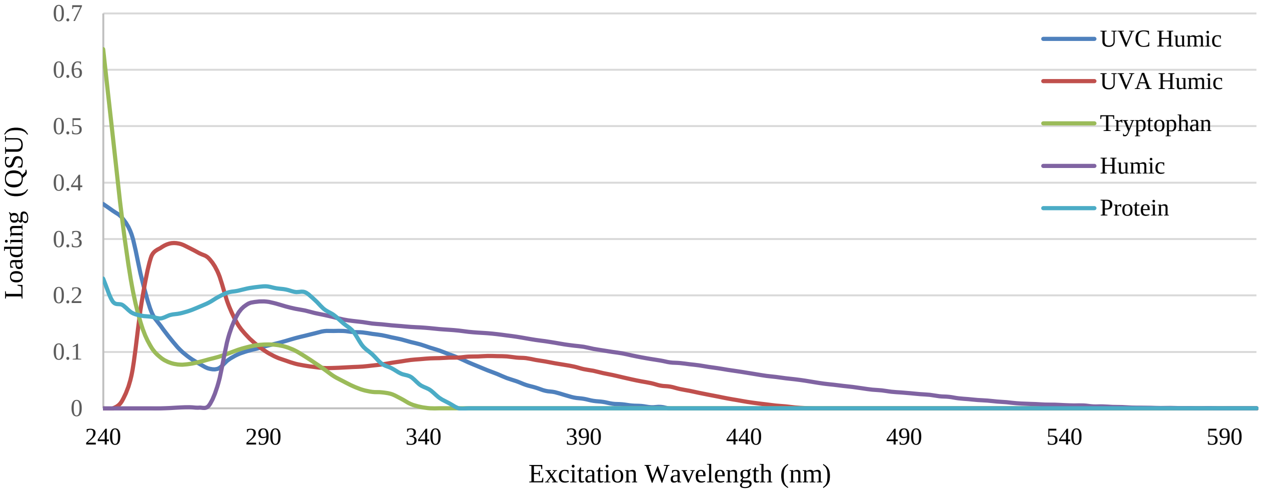

Figure 11 - Excitation loadings (in QSU) for the five-component PARAFAC model derived from 2014 and 2015 Apex River samples.

Appendix D – *Escherichia coli* Results

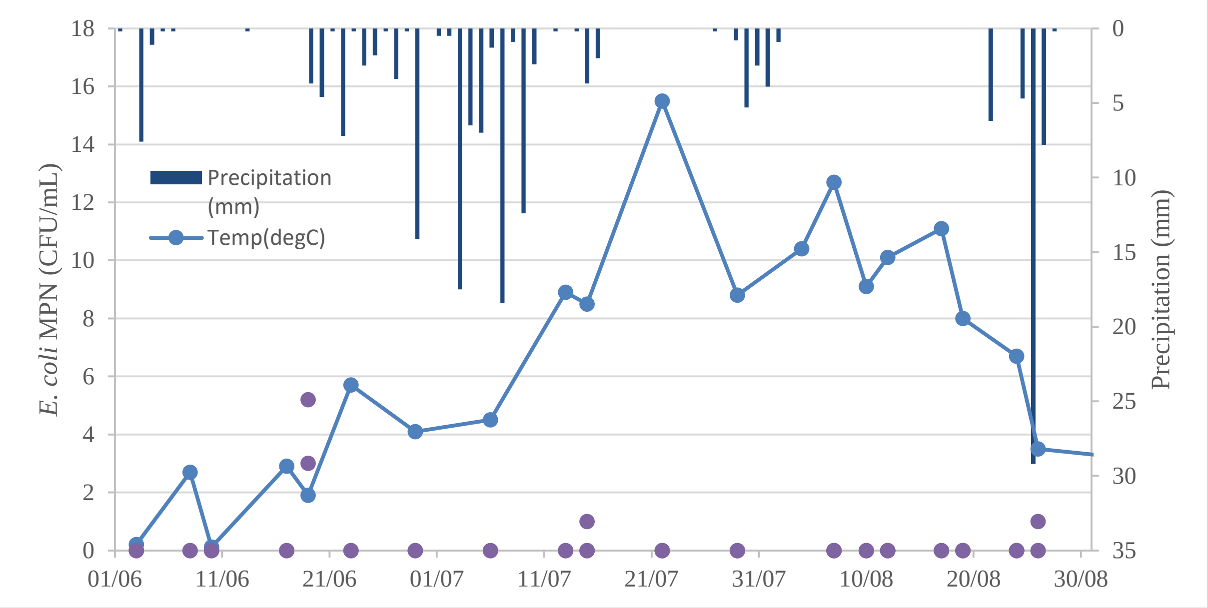

Figure 12 - *E. coli* densities (CFU/mL) and water temperature observed at the CF site during the 2015 ice-free season, plotted with precipitation.