Influence of wildfire and permafrost thaw on dissolved organic carbon (DOC) in northern peatlands; implications for lability and downstream transport.

by

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Abstract

Peatlands in Canada's western boreal forest are a major source of dissolved organic carbon (DOC) to downstream ecosystems, where DOC regulates carbon cycling, and can affect ecosystem productivity and habitat quality. Subarctic ecosystems are becoming increasingly vulnerable to the effects of climate change, particularly to disturbances such as wildfire and permafrost thaw. These disturbances have the ability to alter aboveground vegetation structure, soil thermal regimes, and hydrologic flow paths, and ultimately affect the quantity and composition of exported DOC. In high-latitude regions, the spring freshet is traditionally understudied, yet represents an important component of the annual DOC budget. To better constrain and quantify the impact of wildfire and permafrost thaw on aquatic carbon cycling in boreal peatlands I conducted a first study that comprised three *in-situ* incubation experiments (spring, summer, fall) with porewater collected from a partially burned peatland, investigating how wildfire and permafrost thaw affects DOC susceptibility to microbial and photochemical transformations. In spring, recently thawed sites exhibited greater microbial DOC lability (26% DOC loss) compared to unburned sites with intact permafrost (11%), while sites with mature permafrost thaw or sites that had recently burned both exhibited decreased lability (<5%). All sites exhibited higher microbial lability in the spring than in the summer or fall (2% and 4%, respectively). Also in the spring, microbial lability was strongly correlated to DOC chemical composition, including both its bulk aromaticity and carbon to nitrogen ratio. In contrast, no influence of DOC composition was found on photochemical lability. In a second study, I investigated whether the effects of wildfire on porewater DOC composition were reflected at the catchment outlet. For this, I continuously monitored water chemistry, discharge, and DOC composition at a paired burned and unburned catchment from early spring to fall. Both catchments exhibited similarities in terms of the timing and magnitude of runoff and DOC export; more than 50% of annual DOC export occurred during the spring period. Despite only lasting 8 days, the early spring period exported more than 25% of annual DOC, and this DOC was of particularly high molecular weight and aromaticity. Aside from increased DOC export during the summer at the burned catchment, there was no clear impact of wildfire at the catchment outlet. This suggests that shifting hydrology due to a changing climate may be more important for controlling catchment DOC export than wildfire. Together, our results highlight the potentially opposing effect of wildfire and permafrost thaw on porewater DOC composition, while stressing the importance of the spring period.

Preface

Chapter 2 of this thesis has been formatted and prepared for eventual submission to the *Journal of Geophysical Research: Biogeoscience*, in a collaborative effort between Suzanne Tank, Cristian Estop-Aragonés, David Olefeldt, and myself. I was responsible for experimental design, data collection, data analysis, and manuscript composition. All three co-authors assisted with concept formation, experimental design and site collection, and contributed to manuscript edits and composition.

Chapter 3 of this thesis has been formatted and prepared for eventual submission to *Hydrology and Earth System Sciences*, for the special issue "Understanding and predicting earth system and hydrological change in cold regions". This chapter is part of a larger, nationwide project between the University of Alberta, Government of Northwest Territories, Environment Canada, and Wilfred Laurier University. All co-authors contributed to concept formation and site selection. N. Dion assisted with data collection and analysis, while D. Olefeldt and S. Tank contributed to experimental design and assisted with manuscript edits and composition. I was responsible for data collection and analysis, and manuscript composition.

The literature review in chapter 1 and concluding statements in chapter 4 are my own work.

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Chapter 1: Introduction and Research Objectives

Dissolved organic carbon (DOC) is one of the most dominant forms of carbon in the hydrosphere, and freshwater systems serve to link marine and terrestrial ecosystems (Cole et al., 2007; Holmes et al., 2012). Boreal peatlands located in the discontinuous permafrost zone of western Canada are an important component of terrestrial carbon storage (Tarnocai et al., 2009; Gorham, 1991). These peatlands convey substantial quantities of DOC downstream, where DOC influences ecosystem productivity and greenhouse gas emissions (Sobek et al., 2003; Cory and Kaplan, 2012). Wildfire and permafrost thaw are considered the dominant disturbances associated with a warming climate in boreal peatlands (Tarnocai, 2009). The fate of these ecosystems in light of disturbance remains poorly understood, and subsequent shifts in DOC characteristics on permafrost peatlands may have cascading effects on downstream ecosystems.

1.1 Peatlands in the discontinuous permafrost zone of western Canada

1.1.1 Permafrost peatland formation in western Canada

The Laurentide ice sheet covered much of Canada until 8 kYa BP, when warming during the Holocene initiated glacial retreat (Halsey et al., 1998). The landscape was originally covered in proglacial lakes and rocky landscapes, and it wasn't for another 2000 years that topography, vegetation, and climatic conditions favoured the formation of peatlands in continental western Canada (Halsey et al., 1998; Wieder and Vitt, 2009). Almost all peatlands in the western boreal forest formed through paludification, whereby the absence of standing water led to dry vegetative surfaces conducive to peat formation (Wieder and Vitt, 2009). Initially, these peatlands were permafrost free.

Gradually, *Spaghnum* mosses developed on peatland fens and raised the vegetative surface above the water table – this process insulated the seasonal frost layer from summer thaw (Zoltai, 1995). As the water in the peat froze, frost-heave dynamics forced the vegetative surface even higher above the water table, creating aerobic soil conditions, which support tree growth (Wieder and Vitt, 2009; Zoltai, 1995). Eventually, the trees intercepted enough snow to reduce its insulating effect and the soil water continued to freeze, creating permafrost peat plateaus (Zoltai, 1995). These peatlands are a mosaic landscape comprising young permafrost peat plateaus, permafrost free fens and bogs, and shallow open water (Quinton et al., 2009).

On an annual basis, a portion of frozen surface soil thaws from the top down in the summer due to warm atmospheric temperature; this is known as the active layer. Dry surfaces in the summer months insulate the permafrost from complete thaw, and heat lost through frozen peat in the colder months causes the active layer to refreeze (Zoltai, 1993), allowing the mass of frozen soil to thicken. However, ice can accumulate to a height where the surface is no longer covered by peat, creating deep fissures in the permafrost and subjecting the ice core to thaw (Zoltai, 1993). Once thawed, *Sphagnum* mosses, which rapidly accumulate biomass (Fenner et al., 2004), colonize these ecosystems again, creating aerobic conditions conducive to tree growth; permafrost aggradation and degradation can occur on cycles as low as 600 years (Zoltai, 1993).

1.1.2 Peatland hydrology and function

Aquatic carbon cycling and catchment hydrology is ultimately a function of the interactions between the different land cover types that characterize peatlands. Catchments in the discontinuous permafrost zone of western Canada, or the Taiga Plains, are a mosaic landscape comprising upland forests, permafrost peat plateaus, channel fens, and thermokarst bogs (Quinton et al., 2009). Riparian zones of upland forests generate runoff during periods of hydrologic connectivity; yet can become isolated from the catchment during periods of low flow. Permafrost peat plateaus generate runoff due to their low water holding capacity (Quinton et al., 2009), but as the active layer thaws, the ability of plateau soils to store water increases and thus plateau runoff generation is muted (Quinton and Marsh, 1999). In periods of high flow, bogs are hydrologically connected to surrounding fens, and thus aid in the downstream transport of water (Quinton et al., 2009). However, in periods of low flow, bogs become isolated and typically store water until they are connected again (Quinton et al., 2009). Finally, fens serve to connect plateaus and bogs and convey water downstream to larger stream networks or lakes (Quinton et al., 2009). The percent contribution of these different land covers within a catchment dictates landscape hydrology (Quinton et al., 2009). Northern peatlands are characterized by short summers and long and dry winters, where the majority of precipitation falls as snow (Quinton et al., 2009). Because runoff generation is limited to periods of hydrologic connectivity, these catchments are snowmelt-dominated, with minimal contributions to annual runoff supplied by summer storms (Quinton et al., 2009).

1.1.3 Importance of permafrost peatlands for carbon storage

Peatlands occupy over one million square kilometres across Canada (Tarnocai, 2009), and are found predominantly in the boreal forest. Globally, peatlands are substantial sinks of carbon (Gorham, 1991; Tarnocai, 2009; Turetsky et al., 2007). Permafrost is another global sink of carbon, estimated to contain more than twice as much carbon as the atmosphere (Tarnocai et al., 2009). Up to 37% of Canada's peatlands are underlain by permafrost, primarily in the discontinuous permafrost zone, and in Canada's western boreal forest permafrost peatlands are thought to store 13 Pg C (Vitt et al., 2000; Tarnocai 2009). To put this into perspective, Canada's total greenhouse gas emissions in 2015 were 0.722 Pg CO_2-equivalent (Environment and Climate Change Canada, 2016). Additionally, carbon dioxide emission from freshwater lakes and rivers, which are abundant in peatland systems, is equivalent to carbon transfer from the atmosphere to the earth's surface (Cory et al., 2014). Permafrost peatlands of western Canada are therefore an integral component of the global carbon cycle.

1.2 Disturbances on the Taiga Plains

Climate change has a more pronounced effect on arctic and subarctic regions than anywhere else on the planet, and it is expected that by 2100 these ecosystems will experience an average annual temperature increase of up to 5 °C (IPCC, 2007). In northern ecosystems, wildfire and permafrost thaw are the two largest disturbances associated with warming temperatures (Tarnocai, 2009). Both of these disturbances affect aboveground vegetation composition and structure, impact soil moisture and thermal regimes, and alter catchment hydrology (Turetsky et al., 2002; Flannigan et al., 2008; Quinton et al., 2009; Vonk et al., 2015a; Larouche et al., 2015; Olefeldt et al., 2016).

1.2.1 Wildfire

Warmer temperatures, in conjunction with changing moisture regimes, have played a role in doubling the average annual area burned in western Canada's boreal forest since 1960 (Kaschiske and Turetsky, 2002). Wildfires are a natural stand renewal agent in boreal forests (Flannigan et al., 2008), and are required to maintain ecosystem health and productivity. In North America, more than 75% of all fires larger than 200ha in Canada's Northwest Territories were ignited by lightning in 2015 (Veraverbeke et al., 2017). Observed increases in wildfire over the last half a century are attributed to a lengthened fire season and an increased frequency, severity, and intensity of wildfire in this region (Flannigan et al., 2008; Turetsky et al., 2002), in part due to a significant increase in lightning ignitions since 1975 (Veraverbeke et al., 2017). Wildfires can remove part of the soil organic layer, decrease albedo and alter insolation, enhance soil temperature, consume aboveground biomass, and thicken the active layer of permafrost peatlands (Flannigan et al., 2008, Zoltai et al., 1998). Forest fires in Canada on average release 27Tg C annually, and peat fires, despite occupying a small portion of total Canadian landmass, are responsible for the emission of 6Tg C per year (Flannigan et al., 2008), proving these fires an important component of carbon dynamics and cycling. Wildfires affect biogeochemical dynamics of area burned, and can impact downstream ecosystems (Zoltai et al., 1998). Furthermore, wildfires can also accelerate permafrost thaw due to shifts in soil temperature, vegetation, and hydrologic dynamics (Zoltai, 1993; Zoltai et al., 1998; Tarnocai, 2009). In fact, despite only 25% of the Taiga Plains having burned in the last 30 years, up to 23% of permafrost thaw can be directly attributed to wildfire (Gibson, 2017).

1.2.2 Permafrost thaw

Permafrost thaw is widespread across the circumpolar arctic, but the discontinuous permafrost zone is experiencing thaw at a faster rate than anywhere else (MyClymont et al., 2013). Increasing air and ground temperatures, shifts in evapotranspiration rates, and changes to belowground thermal dynamics has lead to widespread thaw in these ecosystems (Tarnocai, 2009). Because plateaus are raised 0.5-

1.5m above their surroundings (Quinton et al., 2009), thaw causes land subsidence to the elevation of adjacent wetlands (Zoltai, 1993), forming thermokarst wetlands. Thermokarst wetlands impact the hydrology, ecology, and biogeochemistry of northern ecosystems (Olefeldt et al., 2016), by creating anaerobic conditions (Tarnocai, 2009), enhancing the concentration of soil organic carbon in the active layer (Wickland et al., 2007), exposing previously preserved material to surface interactions like decomposition and respiration (Abbott and Jones, 2015), and reactivating groundwater channels (St. Jacques and Sauchyn, 2009). The shifts in surface and subsurface catchment function induced by wildfire and permafrost thaw are likely to impact terrestrial and aquatic carbon cycling in subarctic peatland-rich catchments.

1.3 Dissolved organic carbon

Northern ecosystems transport 110Tg C to either the atmosphere or downstream ecosystems every year (Holmes et al., 2012), yet twice as much DOC is believed to enter inland aquatic ecosystems as is exported out (Cole et al., 2007). Dissolved organic carbon is produced during photosynthesis and is composed of amino acids, carbohydrates, and peptides (Wright and Reddy, 2009). Microbial degradation and organic matter decomposition convert these compounds to humic and fulvic acids, which exist in terrestrial ecosystems and make up the majority of the DOC pool (Corin et al., 1996; Wright and Reddy, 2009). Dissolved organic carbon has many roles in aquatic ecosystems: it is a substrate for microbial growth; a vector for nutrients like nitrogen and phosphorus and contaminants such as methylated mercury; it protects bacteria from UV-radiation; and, due to its tea colour, affects the depth light can penetrate in downstream lakes (Cory et al., 2014; Wright and Reddy, 2009; Obernsterer and Benner, 2004; Sulzberger and Durisch-Kaiser, 2009).

1.3.1 Sources of DOC

Water traveling through organic-rich soil horizons in riparian zones in upland forests and peatlands, and subsurface mineral horizons brings DOC into freshwater ecosystems in peatland complexes (Ledesma et al., 2017; Ågren et al., 2008; Kaiser and Kalbitz, 2012). Dissolved organic carbon originating from organic soils on peat plateaus and upland forest riparian zones is typically aromatic, due to the humified nature of peat (Selvam et al., 2017). Because thermokarst bogs are characterized by non-vascular plant species like *Sphagnum riparium* or *Sphagnum fuscum*, and these moss roots exude DOC that is typically aliphatic in structure (Spencer et al., 2008). Aliphatic DOC originating off of thermokarst bogs is considered fresh, as it has been exposed to limited degradation before entering the hydrosphere. Groundwater traveling through mineral soil horizons can also convey DOC towards the catchment outlet, and this DOC differs from organic soil DOC in both concentration and composition. As DOC percolates downward through mineral horizons, large aromatic compounds adsorb to or co-precipitate out of the soil, and remaining compounds are subjected to substantial microbial processing (Kaiser and Kablitz, 2012). Once mineral soil DOC reaches the catchment outlet, it is aliphatic in structure due to the loss of aromatic compounds, and exists in much lower concentrations (Kaiser and Kablitz, 2012). While mineral soil DOC and thermokarst bog DOC may appear similar in composition, they differ in availability to microbes in downstream ecosystems.

The relative contribution of these three DOC sources to the catchment outlet is dependent on hydrologic connectivity, which is primarily a function of season. Runoff generation, which is tightly linked to DOC export (Clark et al., 2007), is dominated by spring snowmelt in northern high-latitude regions (Quinton et al., 2009). During periods of high flow, peatland complexes and upland forests are hydrologically well connected to downstream ecosystems, and thus contribute DOC to the catchment outlet (Fellman et al., 2009). In periods of low flow, however, upland forests and thermokarst bogs become hydrologically isolated from their surroundings (Quinton et al., 2009), and the contribution of organic soil DOC to downstream ecosystems is dominated by subsurface flow in permafrost peatlands. Mineral soil DOC, although in low concentrations, is of greater importance after spring snowmelt, when groundwater connectivity generates runoff. We therefore see highly aromatic DOC from near surface organic soils exported during the spring, and lower aromaticity due to groundwater influence during the summer and fall (Fellman et al., 2009; Kaiser and Kablitz, 2012; Olefeldt and Roulet, 2014).

1.3.2 DOC transformations

The source of DOC governs its composition, which determines its susceptibility to transformations within the water column (Wright and Reddy, 2009; Corin et al., 1996). There are two primary pathways of DOC transformation in aquatic ecosystems: photochemical processing and microbial degradation (Sulzberger and Durisch-Kaiser, 2009; Wright and Reddy, 2009; Obernosterer and Benner, 2004; Lennon and Pfaff, 2005). Together, these processes account for up to 90% of DOC transformation in the water column, and produce more than a third of CO_2 released from inland waters (Cory et al., 2014). While determining exact DOC composition is difficult, optical properties enable the determination of bulk DOC characteristics: specific UV-absorbance (SUVA) at 254 nm, normalized to DOC concentration, has been linked to DOC aromaticity (Weishaar et al., 2003), while the slope of absorbance between 275-295 nm is inversely related to a compound's molecular weight (Fichot and Benner, 2012). Photochemical processing affects primarily large, degraded, and tightly conjugated aromatic DOC structures, while microbes prefer small, fresh, aliphatic DOC compounds (Sulzberger and Durisch-Kaiser, 2009; Obernosterer and Benner, 2004; Cory et al., 2014; Corin et al., 1996). Therefore, DOC originating from permafrost peatlands and riparian zones, because this DOC is aromatic, is available for photochemical degradation, and fresh root exudates originating from thermokarst bogs, and to a lesser extent, peat plateaus, is microbially labile. Although mineral DOC is aliphatic, because it has been subjected to substantial microbial processing within the soil horizon, this DOC is microbially recalcitrant (Kaiser and Kablitz, 2012). Due to the lack of aromatic compounds, mineral soil DOC at the catchment outlet is also photochemically recalcitrant.

Because wildfire and permafrost thaw affect vegetation and soil physiological properties, they can impact DOC production and decomposition (Vonk et al., 2015a; Larouche et al., 2015; Olefeldt et al., 2013; Quinton et al., 2009; Flannigan et al., 2008), which in turn may impact DOC lability to photo and microbial degradation. For example, burning organic matter removes carboxyl groups from the DOC pool (Hauimeier and Zech, 1995), a group of carbon moieties that has been shown to be disproportionately susceptible to photodegradation (Ward and Cory, 2016). In contrast, young thermokarst bogs are characterized by *Sphagnum riparium*, a moss that produces non-structural carbohydrates highly susceptible to biodegradation (Turetsky et al., 2008).

1.4 Importance of our research

Studies conducted in the circumpolar arctic have researched the influence of wildfire or permafrost thaw on DOC susceptibility to transformations (Selvam et al., 2017; Vonk et al., 2015, and references within; Olefeldt et al., 2013a; Olefeldt et al., 2013b). However, these studies have failed to examine the interactive effects of these disturbances and seasonality on DOC degradability in downstream ecosystems. Furthermore, due to the remote location of northern research sites, data collection is limited by accessibility, and samples are obtained at large return intervals, which may not accurately capture DOC dynamics (Strohmeier et al., 2013; Clark et al., 2007). Additionally, the spring freshet continues to be a traditionally understudied time frame (Finlay et al., 2006), despite its implications for annual DOC cycling. We are the first study conducted on the Taiga Plains that has examined the combined effect of wildfire, permafrost thaw, and seasonality, on DOC composition and degradability. We are also one of the first studies to capture the entire spring freshet with continuous data collection, which allows us to examine the influence of disturbance and seasonality on DOC cycling at the catchment scale.

With a warming climate, the incidence and intensity of wildfires and prevalence of thaw features on the landscape are expected to increase well into the next century (Flannigan et al., 2008; Tarnocai, 2009; Schuur et al., 2000). These disturbances have been shown to induce shifts in DOC composition and export in downstream aquatic eocsystems (Vonk et al., 2015 and references within; Olefeldt et al., 2013b), which likely impacts regional ecosystem productivity and greenhouse gas emissions. Because freshwater ecosystems are an often-overlooked component of larger carbon scales (Cole et al., 2007), our research aims to improve our understanding of the fate of these ecosystems under a warming climate. Finally, the catchments in which we conducted our research provide drinking water for small indigenous communities, and shifts in DOC composition are likely to impact drinking water quality.

1.5 Research questions and hypotheses

Peatlands are responsible for the storage and export of up to one third of the world's carbon (Gorham, 1991), and wildfire and permafrost thaw in subarctic and arctic regions are disturbing the equilibrium and balance of these ecosystems. Because the frequency of disturbance on these vulnerable landscapes will continue to increase with climate change, it is paramount to better understand the effects of disturbance at the catchment scale so we are better equipped to make predictions for future carbon cycling at a global My thesis is divided into two research chapters. The second chapter of my thesis provides valuable insight into the combined effects of photochemical and microbial transformations, and how disturbances on the Taiga Plains influence DOC susceptibility to degradation. I conducted this research to answer the following research questions:

1. Do wildfire and permafrost thaw affect the composition of DOC exported off of peatlands on the Taiga Plains? and,
2. if yes, do changes to DOC composition affect its lability to photochemical and microbial degradation?

Prior to conducting this research I hypothesized:

H_1: Permafrost thaw creates land subsidence and waterlogged conditions, resulting in slower rates of decomposition, coupled with vegetative shifts towards *Sphagnum riparium* (Fenner et al., 2004; Kokelj and Jorgenson, 2013) – and we therefore hypothesize that thermokarst wetlands will export nonaromatic DOC. Wildfire can burn off the upper peat layer and remove surface vegetation, thereby producing char and reducing primary productivity (Flannigan et al., 2008; Olefeldt et al., 2013a) – and we therefore hypothesize that wildfire will enrich affected areas with aromatic DOC.

H_2: Through the production and enhancement of highly aromatic compounds, but loss of photolabile DOC compounds on burned plateaus, we hypothesize wildfire will reduce DOC biodegradability, and will reduce DOC photolability when compared to intact peat plateaus. We hypothesize that permafrost thaw will enhance DOC biodegradability but will not affect its photolability (Table 1.1). Regardless of disturbance, plateaus will naturally have lower biodegradability than young thermokarst wetlands due to the highly decomposed nature of peat.

The third chapter of my research focuses on the effect of disturbance on catchment ecosystem hydrology and function. Chapter 3 compares DOC concentration, absorbance, and discharge at a paired burned and unburned catchment outlet with similar landscape cover to examine the effect of wildfire on downstream ecosystems. I conducted this research to answer the following questions:

3. If we do not reject H_1, are the effects of changes to DOC composition reflected at the catchment outlet?
4. Does wildfire impact runoff and/or DOC export?

Prior to conducting this research I hypothesized:

H_3: If we do not reject H_1, we will observe higher aromaticity at the outlet of the burned catchment when compared to the unburned catchment, which will likely influence DOC transformative processes.

H_4: Wildfire reduces surface vegetation and evapotransporation (Flannigan et al., 2008), providing greater quantities of water available to runoff, and thickens the seasonally thawed layer (Gibson, 2017) exposing deeper sources of DOC. We hypothesize that wildfire-affected catchments will have enhanced runoff generation and DOC export.

Table 1.1. We designed our first experiment to collect water from three spots along a paired burned and unburned transect (plateau, edge, bog). Sites were analyzed based on whether they had burned, thawed, or both burned and thawed. We then hypothesized the susceptibility of DOC exported off of each site to microbial and photochemical transformations.

Location	Disturbance		Lability to Transformation	
	Burn	Thaw	Microbial	Photochemical
Plateau			Low	Very High
Young Thermokarst Bog		X	High	Low
Mature Thermokarst Bog			Low	Low
Burned Edge	X	X	Intermediate	Intermediate
Burned Plateau	X		Very Low	High

Chapter 2: Interactive effects of wildfire, permafrost thaw, and season on the lability of dissolved organic carbon from boreal peatlands.

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Abstract

Boreal peatlands are major sources of dissolved organic carbon (DOC) to downstream freshwater systems, where DOC plays an important role in regulating carbon cycling. Wildfire and permafrost thaw cause shifts in peatland vegetation and hydrology, and may have cascading effects on downstream ecosystem functions. Here, we examined the influence of wildfire and permafrost thaw on susceptibility of peatland porewater DOC to microbial and photochemical transformations, assessed through seven-day *in-situ* pond incubations carried out in spring, summer, and fall. In spring, when the peatland was hydrologically connected to the catchment stream network, sites with recent permafrost thaw had high microbial DOC lability (17-26% loss) compared to unburned sites with intact permafrost (11%), while sites recently burned or with mature thaw had low lability (<5%). Microbial lability in spring was strongly associated with the C/N ratio and aromaticity of DOC. No difference in microbial DOC lability among sites was found in later seasons, and overall lability was reduced compared to spring (average 2% and 4% DOC loss across sites in summer and fall, respectively). There was no significant difference among sites in DOC loss attributed to photochemical degradation, and all samples were diluted to a similar absorbance, but results suggested that photochemical processes contribute considerably to DOC mineralization in shallow peatland ponds. Our results thus highlight similarities and differences in potential effects of peatland wildfire and permafrost thaw on the functioning of downstream aquatic ecosystems, and stress the importance of the spring period.

2.1 Introduction

Up to 200 Tg dissolved organic carbon (DOC) enters inland aquatic ecosystems every year, yet only half of it reaches the Arctic Ocean (Cole et al., 2007; Holmes et al., 2012), proving freshwater ecosystems an important component of the global carbon cycle. Particularly of importance are subarctic, carbon-rich ecosystems dominated by peatlands, which control catchment composition and concentration of exported DOC (Ågren et al., 2008). While in transit between terrestrial and marine ecosystems, DOC is subjected to photochemical and microbial transformations such as mineralization; the rate at which these transformations occur is dependent upon DOC concentration and chemical composition (Sobek et al., 2003; Cory and Kaplan, 2012). High-latitude arctic ecosystems are experiencing the effects of climate change more than anywhere else on the planet (IPCC, 2007), and in the discontinuous permafrost zone of western Canada, major disturbances such as wildfire and permafrost thaw (Tarnocai, 2009) may alter DOC susceptibility to transformations. Climate change thus could have a cascading affect on aquatic carbon cycling (Lundin et al., 2016). Runoff generation in northern ecosystems is snowmelt dominated (Quinton et al., 2009), and therefore seasonality plays an important role in dictating downstream ecosystem function. Shifting DOC lability in response to disturbance in the discontinuous permafrost zone has potential implications for the global carbon cycle, yet the effect on downstream ecosystems remains unknown.

Catchments in the discontinuous permafrost zone of western Canada, or the Taiga Plains, are a mosaic landscape consisting of upland forests, permafrost peat plateaus, permafrost-free channel fens and thermokarst bogs, and shallow open water wetlands (Quinton et al., 2009). Dissolved organic carbon export is dictated by runoff (Clark et al., 2007), the timing and magnitude of which is dependent on hydrologic connectivity (Olefeldt et al., 2013b) and landscape cover (Quinton et al., 2009). The spring freshet dominates runoff production in high-latitude regions (Quinton et al., 2009), during which time low concentration aliphatic and biodegradable DOC is exported in high quantities in peatland and boreal systems (Broder et al., 2017; Ågren et al., 2008). Due to lower hydrologic connectivity and longer water residence times, DOC exported in the summer and fall is aromatic and exported in minimal quantities due to limited runoff production (Broder et al., 2017; Ågren et al., 2008). While the influence of seasonality on DOC characteristics has thus been extensively studied, no study has looked at the interaction between disturbance and seasonality on boreal peatlands.

On the Taiga Plains, wildfire and permafrost thaw are considered the two major disturbances associated with climate change (Tarnocai, 2009). Wildfires can remove surface vegetation and the upper peat layer, and enrich burned peat plateau soils with aromatic carbon compounds (Flannigan et al., 2008; Olefeldt et al., 2013a). By altering albedo and soil temperature (Flannigan et al., 2008; Zoltai et al., 1998), wildfire can induce permafrost thaw: despite only 25% of the Taiga Plains having burned in the last 30 years, 23% of thaw can be attributed to wildfire (Gibson, 2017). Permafrost thaw, whether triggered by climate warming or directly by wildfire, causes land subsidence, which changes hydrologic connectivity (Zoltai, 1993; Tarnocai, 2009) and shifts treed peat plateaus into moss-dominated thermokarst bogs (Kokelj and Jorgenson, 2013). Previous studies have determined that thermokarst bogs may produce highly labile DOC (Selvam et al., 2017), yet have failed to examine the additional interactive effects of seasonality and wildfire.

Elucidating specific DOC composition is difficult, yet bulk characteristics can be determined through proxies like specific UV-absorbance (SUVA) or carbon to nitrogen ratio (C/N); the former is positively correlated to aromatic carbon content, while the latter is related to degree of decomposition of source material (Weishaar et al., 2003; Pinsonneault et al., 2016; Fellman et al., 2008; Kuhry and Vitt, 1996). Dissolved organic carbon originating from soil leachates on peat plateaus is aromatic and humified (Olefeldt et al., 2013b; Wright and Reddy, 2009), and has been found to be a poor quality resource for aquatic bacteria (Lennon and Pfaff, 2005). Root exudates exude DOC from non-vascular plants, and this DOC is typically more biodegradable than DOC originating from woody biomass (Pinsonneault et al., 2016; Spencer et al., 2008). Microbes preferentially consume aliphatic, fresh DOC, and thus both SUVA and C/N have been found to be negatively correlated to DOC biodegradability (Pinsonneault et al., 2016; Fellman et al., 2008; Weishaar et al., 2003). UV-degradation targets aromatic DOC (Corin et al., 1996), yet specific aromatic compounds - such as lignin vs. char - may have different light-absorbing properties (Haumaier and Zech, 1995); and therefore photolability must be defined as a function of photons absorbed, or apparent quantum yield (Cory et al., 2013). Wildfire removes the carboxyl moieties from the DOC pool (Haumeier and Zech, 1995), a form of carbon that has been shown to be more susceptible to photodegradation than aromatic or phenolic compounds (Ward and Cory, 2016). While microbial degradation selectively enhances the DOC pool with aromatics (Wickland et al., 2007), photochemical degradation can cleave DOC into small, biodegradable compounds (Jorgenson et al., 1998). Together, photochemical and microbial degradation can transform up to 90 % of DOC in transit through northern ecosystems (Cory et al., 2014). However, in addition to composition, DOC susceptibility to transformation is also dependent on previous exposure to light and processing (Cory et al., 2014; Selvam et al., 2017). Wildfire and permafrost thaw can therefore alter rates of DOC degradation through shifts in vegetation and rates of DOC production (Fenner et al., 2004), or exposing previously frozen DOC to surface processes (Abbott and Jones, 2015).

We conducted incubation experiments at three different times during the growing season using porewater collected from a partially burned peatland catchment to examine the effect of wildfire, permafrost thaw, and seasonality on DOC characteristics and susceptibility to photochemical and microbial degradation. We expect that permafrost thaw will enhance DOC biodegradability, while wildfire will have the opposite effect. We hypothesize that wildfire will also produce less photolabile DOC compounds, thereby reducing photochemical degradation on burned peat plateaus, when compared to intact peat plateaus. However, we expect greater photolability on peat plateaus, both burned and unburned, when compared to thermokarst bogs. Furthermore, we expect that the influence of disturbance will be greatest when hydrologic connectivity is highest, and upstream systems can connect to and flush DOC downstream. Our study aims to help us better understand how wildfire and permafrost thaw will influence carbon cycling in the discontinuous permafrost zone of western Canada, to better project impacts on carbon cycling in downstream aquatic ecosystems.

2.2 Methods

2.2.1. Study site and porewater sampling

We selected a peatland complex consisting of peat plateaus and thermokarst bogs in the boreal discontinuous permafrost zone of the Northwest Territories, Canada (61°20’N, 120°08’W). The peatland was partially affected by fire in 2013, which burned some the peat plateau area but did not affect thermokarst bogs, due to their wetter soils and lack of tree cover (Table 2-1). The climate of the region is characterized by short summers and long and dry winters. Historical average annual temperature is -3.2 °C and the annual precipitation is 369 mm, of which 46% is snow (Quinton et al., 2009; Meteorological Service of Canada, 2011).

Two sampling transects were established 800 m apart in the peatland complex, one in a section affected by wildfire and one outside the fire boundary (Figure 1). The sampling sites varied with regards to dominant vegetation, near-surface peat type, permafrost conditions and history, and water table position (Table 1). Each transect was approximately 70 m in length and the unburned transect included a peat plateau site (P), a recently thawed site at the permafrost edge between the peat plateau and thermokarst bog (YB), and a mature thermokarst bog site (MB) (Figure 2). Peat depth was ~265 cm at the mature bog. The unburned plateau site had an open canopy of ~5 m tall black spruce (*Picea mariana)* and an understory dominated by labrador tea (*Rhododendron groenlandicum*) and lichens (*Cladonia spp.*) (Figure 2-2). The young thermokarst bog was dominated by *Sphagnum riparium* and water sedge (*Carex aquatilis)*. The young thermokarst bog formed approximately 90 years BP, as indicated by peat cores taken at a nearby catchment (61°18′N, 121°17′W) (Pelletier et al., 2017). The burned transect consisted of a burned plateau (BP), a recently thawed site at the boundary between the peat plateau and thermokarst bog with evidence that thaw occurred after the wildfire (BE), and a mature bog. At the mature thermokarst bog, peat was found to a depth of 290 cm. Vegetation at the two bog sites was similar and dominated by *Sphagnum fuscum* and leather-leaf shrubs (*Chamaedaphne calyculata*). There was no evidence of wildfire at the mature bog within the burned transect (Table 2-1), and the presence of *Sphagnum fuscum* at both bogs indicates that permafrost has been absent at least 100 years (Pelletier et al., 2017). The burned edge site is likely to have undergone permafrost thaw in the last 3 years since the wildfire, since the ground cover is identical to the burned plateau site but the peat surface is now subsided and waterlogged (Figure 2-2). All black spruce were dead at the burned plateau site, and the ground was charred with sparse labrador tea.

Porewater collection was carried out in spring (May 21), summer (July 18), and fall (September 12) in order to determine seasonal changes on porewater chemistry, DOC composition and its lability. The spring sampling occurred during the receding limb of snowmelt freshet in the region (Figure 3) and it is likely at this time that surface water in the peatland complex was hydrologically connected to the catchment stream network, considering the shallow water table in the sampling sites. Heavy storms during summer and fall can contribute significantly to the annual runoff generation in the region (Clark et al., 2007), but in 2016 there were no major storms, suggesting peatland hydrological connectivity to the catchment stream network after the spring sampling period was likely limited.

Porewater was collected using MacroRhizon soil porewater samplers with a 0.15 μm pore size (Rhizosphere Research Products, Wagening, the Netherlands), inserted into the soil near the surface to collect samples more likely to be exported during runoff and advection. Because hydrological conductivity decreases with peat depth, most runoff generated from peatlands occurs near the water table, and therefore surface porewater is representative of the DOC that is potentially exported to streams. Soils near the surface were drier at the plateau and burned plateau sites, which required removal of surficial peat and deeper insertion of samplers (~10-30 cm depending on season), to obtain porewater. In each site, porewater was obtained from three locations (5-10 m apart from one another), to account for site spatial variability, and pooled into a single sample until a sufficient volume (~2 L) was collected for analysis and incubation preparations. Samples were kept cool and dark in 4 L polyethylene bottles overnight. Because there was no evidence of fire at the mature bog in the burned transect, porewater collected at both transects was pooled to create one mature bog sample prior to dilution.

2.2.2 Porewater analysis

Samples were obtained from the polyethylene bottles for physico-chemical analyses. Absorbance between 230 and 600 nm was determined in the field in a quartz cuvette using a UV-vis portable spectrometer (Flame-DA-CUV-UV-VIS, Ocean Optics, Dunedin, FL, US). This was required to prepare the incubations (see below). Another subsample was transferred into a 60 mL amber glass bottle and acidified with 0.6 mL 2 N HCl^- for subsequent lab analysis of DOC, and total dissolved nitrogen (TDN). Analysis for DOC and TN concentrations were carried out within 8 days of subsampling on a TOC-L combustion analyzer: concentration measurements are based on four injections, where the average standard deviation for injections of the same sample was 0.07 mg C L^{-1} and 0.008 mg N L^{-1} (Shimadzu, Kyoto, Japan). Also at each location, prior to being pooled, 60 mL of water filtered to 0.15 µm was collected and stored in amber glass bottles to analyze for total dissolved phosphorous (TDP), and major anion and cation (Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, SO_4^{2-}, and sum of Fe^{2+} and Fe^{3+}) concentrations. Concentration of TDP was determined utilizing standard acid hydrolysis methods (4500-P-B) for flow-injection analysis (American Water Works 2004), with concentrations determined based on the stannous chloride method. Major ion concentration was determined by ion chromatography, as defined by Method 300 (Environmental Protection Agency, 1999).

2.2.3 Incubation

Seven day incubation experiments of the peatland porewater samples were carried out in a 0.1 ha shallow pond (59.48 ˚N, 117.18 ˚W) to determine the interactive effects of site and season on DOC lability as assessed under dark (microbial DOC mineralization) and light (combined photochemical and microbial DOC mineralization) treatments. Incubations were initiated the day after porewater collection. Using the measured absorbance from collected porewater, samples were diluted with aerated (O_2 saturated) 0.001 N $NaHCO_3$ solution to an absorbance of 0.35 m^{-1} at 254 nm. This dilution was done to standardize and buffer pH among samples, to standardize DOC concentrations (7-17 mg C L^{-1}) among samples, in order to reduce conditions of anoxia during the incubation time, and to ensure that light-exposed samples of the same incubation absorbed the same amount of sunlight, effectively addressing the idea of apparent quantum yield. Diluted samples were further inoculated at a 1 % volume ratio with a mixed solution of stream water and peatland porewater filtered using 1.6 µm pore size glass microfibre filters (Grade GF/A, Whatman) aiming to standardize the microbial community among samples, while excluding microbial grazers. Then, ultra-violet (UV) light transparent 1L Tedlar bags (Keika Ventures, North Carolina, USA) were filled with 400 mL of the prepared sample to be deployed in the pond. Five replicates per site were prepared for dark treatments (Tedlar bags covered with duct tape) and another five replicates per site were prepared for the light treatments. Due to the pooling of porewater collected from both mature bog sites, eight replicates were prepared for dark treatments and another eight replicates were prepared for light treatments.

A 60 mL and a 15 mL sample were drawn from each replicate prior to pond deployment (day 0) and also at the end of the incubation (day 7). The 60 mL sample was acidified with 0.6 mL 2 N HCl^- to inhibit further microbial DOC mineralization, and stored in cool, dark amber bottles until being analyzed for DOC and TN within eight days of collection, as described above. The 15 mL sample was filtered with 0.7 µm glass microfiber filters (Grade GF/F, Whatman) and analyzed immediately for absorbance spectra as described above. The Tedlar bags were placed submerged in floating mesh baskets within the pond during the incubation experiments. Bags were submerged 10 cm during the spring incubation and 2 cm during the summer and fall incubations. There was no evidence of a treatment effect (light vs. dark) when the bag was submerged at 10 cm, and thus we assumed losses in both the light and dark treatment in the spring were attributed to microbial degradation only. Pond water temperature (HOBO pendant temperature logger, Onset, MA, US) and incoming photosynthetically active radiation (PAR), which we assume to be proportional to incoming UV-light, above the water surface (Photosynthetic Light Smart Sensor, Onset, MA, US) were monitored during the incubation time. Our experimental design is not predicated on being able to determine the precise amount of UV-light absorbed, rather absorbance was standardized among all samples, and therefore we instead tested for differences in UV lability (see below). Water temperatures averaged 14, 21, and 11 °C for the spring, summer, and fall incubations, respectively, while incoming PAR averaged 420 and 210 µmol m^{-2} s^{-1} during the summer and fall incubations, respectively.

2.2.4 Data reporting and statistical analysis

Specific UV absorbance at 254 nm (SUVA) is a measure of DOC aromaticity and was calculated by dividing decadic absorbance at 254 nm with DOC concentration (Weishaar et al., 2003). The quenching of absorbance due to iron (Fe) (Poulin et al., 2014) was ruled out since maximum Fe:DOC was 0.02. The porewater C/N ratio was calculated using the molar ratio of DOC and TDN. Loss of DOC during the incubations was calculated as the difference between DOC concentration at day 0 and 7 of the incubation. For the dark treatment, we define DOC biodegradability (BDOC) as the percent DOC loss during the incubation relative to the initial concentration. Light treatment DOC loss is considered a combined effect of direct photochemical DOC mineralization and stimulated microbial mineralization, because we did not remove microbes from the light treatments. Photochemical mineralization is calculated by subtracting site-wide averages of dark losses (dark incubation) from site-wide average of light losses (light incubation). There was no significant effect of site on DOC loss in summer or fall (ANOVA, $p > 0.05$), and differences in DOC loss between season and treatment was assessed using a two-way ANOVA to test the effects of treatment, season, and their interaction. Data was checked for normality (Shapiro-Wilk test for Normality) and homogeneity (Levene's test) (RStudio 0.99.903), and least square mean differences were calculated with Tukey's HSD test.

2.3 Results

2.3.1 Porewater chemistry and DOC composition

Seasonal differences in porewater DOC characteristics and nutrient concentrations between the sites are shown in Figure 2-4. Porewater DOC concentrations, SUVA, and C/N generally increased from spring to fall, with the greatest change occurring between spring and summer in most sites. The exception was YB, which had consistently high DOC concentration and showed distinctive values in spring – greatest DOC and TDP, lowest SUVA and C/N ratios relative to the other sites. The wildfire-affected sites had higher SUVA and C/N ratios than their paired unburned sites (P vs. BP, YB vs. BE) during the spring period. Concentrations of TDP were variable both between sites and seasons (Figure 2-4d). Burned and recently thawed sites had high TDP, particularly in spring, while TDP remained < 50 µg L^{-1} throughout the study at P and MB. With the exception of BP, TDP decreased from spring through summer and fall. Cations concentration also increased with time in most sites, except at YB, where values were distinctly higher in spring relative to other sites (Figure S2-1). Combined cations concentrations ranged from 8 - 30 mg L^{-1}, and were consistently highest at YB. Electrical conductivity ranged from 38 - 62 µS cm^{-1}, and pH ranged from 3.8 - 4.2 (Figure S2-5), meaning all sites are largely ombotrophic with minor groundwater connectivity.

2.3.2 Biodegradability

Initial decadic absorbance at 254nm (A_{254}) of the undiluted samples ranged from 1.13 - 2.52 m^{-1} in the spring, 2.02 - 6.27 m^{-1} in the summer, and 1.96 - 7.32 m^{-1} in the fall; after dilution A_{254} ranged from 0.33 - 0.38, 0.33 - 0.43, and 0.32 - 0.41 m^{-1} in the spring, summer, and fall, respectively. Initial DOC concentration of the diluted samples ranged from 9.17 - 18.5 mg C L^{-1} in the spring, 6.95 – 12.2 mg C L^{-1} in the summer, and 7.62 - 13.3 mg C L^{-1} in the fall. The greatest BDOC observed in the dark incubations occurred in the spring, especially in the YB, and to a lesser extent BE, sites of recent permafrost thaw (Figure 2-5). The smallest BDOC occurred in MB, with little change between seasons. There were statistically significant differences in BDOC between sites and seasons, although these main effects are interpreted in the context of the statistically significant interaction between both factors by using a post hoc Tukey HSD test (Table 2-2). In spring, BDOC in YB (26.2 ± 2%) was significantly greater than the rest of the sites, and BDOC in BE (15.5 ± 4%) was significantly greater than BDOC in P (10.1 ± 2%), BP (5.6 ± 2%), and MB (4.5 ± 2.) (Figure 2-5, Tables S2-3 and S2-4).

There was a significant negative exponential correlation between BDOC and C/N ($R^2 = 0.95$, $p = 0.002$) and a significant, negative logarithmic correlation between BDOC and SUVA ($R^2 = 0.78$, $p = 0.028$) during the spring incubation (indicated by solid lines), but there was no correlation between BDOC and either index in the summer or fall (Figure 2-6). In the spring, BDOC was also positively linearly correlated to TDP concentration ($R^2 = 0.81$, $p = 0.036$, Table S2-2). These relationships were not observed in the summer or fall, when porewater had generally high SUVA, high C/N, and low BDOC (Figure 2-4). No significant relationships were observed between the sampled ions (Cl^-, SO_4^{2-}, Al^{3+}, $Na^=$, $K^{+,}$, Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$) and BDOC (Table S2-2).

2.3.3 Photolability

Light treatment incubations losses (0.75 ± 0.3 mg C L^{-1}) were significantly greater than dark treatment incubation losses (0.32 ± 0.2 mg C L^{-1}, $p < 0.0001$). Light treatments account for both types of degradation (photochemical and microbial). Microbial losses were greater in the fall but total losses were greater in the summer (Figure 2-7), which suggests that photochemical and photochemically enabled microbial losses work together to enhance DOC degradation. In the dark incubations, DOC loss is attributed only to microbial degradation; photochemical losses are then calculated as the difference between losses in light and dark treatments. Biodegradability of carbon can be expressed as a percent; photodegradation is expressed as an absolute value. Incoming PAR doubled in summer (422 ± 160 µmol m^{-2} s^{-1}) in comparison to the fall (214 ± 140 µmol m^{-2} s^{-1}), and nearly twice as much DOC loss was attributed to photodegradation in the summer (0.59 ± 0.2 mg C L^{-1}), than in the fall incubation (0.36 ± 0.1mg C L^{-1}, Figure 2-7). However, this difference was not statistically significant between seasons (paired t-test, p = 0.074). Absolute DOC loss under light treatment was not significantly correlated to SUVA ($R^2 < 0.5$, $p > 0.05$) or C/N ($R^2 < 0.5$, $p > 0.05$). Furthermore, there were no site-specific effects on photodegradation (ANOVA, $p > 0.05$ in summer and fall), and the patterns observed when examining biodegradability, such as differences between burned and unburned sites, did not emerge (Figure S2-2). Replicates from each site were subjected to light losses, yet due to the lack of site-specific effects (t-test, $p > 0.05$), results are pooled by season.

2.4 Discussion

2.4.1 Peatland porewater characteristics

We found strong seasonal shifts in DOC characteristics across sites, and there were indications that the effects of wildfire and permafrost thaw on DOC characteristics were dependent on season. Most pronounced differences between sites were found in spring, when YB exhibited much higher DOC concentration, with lower SUVA and C/N ratio than in other sites. In contrary, fire was indicated to increase DOC aromaticity and C/N ratio. These differences were however lesser or non-existent during summer and fall. In general across sites we observed increasing DOC concentrations, DOC aromaticity, and C/N ratios from spring to summer through fall.

Peatland runoff affected by disturbance may also influence downstream carbon cycling due to altered nutrient export. At undisturbed sites (P, B), we found very low TDP concentrations (Figure 2-4d). Because most available phosphorus is consumed by vegetation, there is low potential for phosphorus export off of undisturbed plateaus and bogs. In contrast to the undisturbed sites, we observed enhanced TDP concentrations in sites that had thawed, burned, or thawed and burned (Figure 2-4d). Unlike other nutrients, phosphorus is not volatized during a wildfire and thus its pool is not reduced after soil burns (Smith et al., 2001). Additionally, if the burn causes the loss of aboveground vegetation (Flannigan et al., 2008), there is no primary productivity on burned plateaus, and thus no phosphorus uptake. Increased phosphorus export off of recent thermokarst in upland regions has also been previously documented, yet its effect on downstream ecosystems still remains relatively unknown (Abbott et al., 2014). However, it is possible that the increased release of phosphorus off of burned plateaus and recent thermokarst could enhance downstream productivity, or - when severe - lead to eutrophication.

2.4.2 Effects of season, fire, and permafrost thaw on porewater DOC biodegradability

Biodegradability, with the exception of MB and BP, was greatest in the spring (Figure 5). Early in the ice-free season, the biologically available component of DOC was likely high due to the combined effect of lower biotic turnover rates and biotic demand under lower temperatures, which leads to a build-up of biologically available DOC over the winter (Fellman et al., 2009; Haei et al., 2012). Additionally, because the water table is closest to the surface in the spring (Table 2-1), shallow flow paths bypassing aromatic DOC in subsurface soils in peat plateaus or riparian zones (Broder et al., 2017) likely also enhanced springtime biodegradability. Wildfire caused shifts in DOC composition that resulted in decreased biodegradability, while permafrost thaw had the opposite effect (Figure 2-5).

We observed increased SUVA and C/N at burned sites, suggesting wildfire directly alters carbon composition (Figures 2-6a and 2-6b). Increased SUVA after a fire has been observed in studies conducted in permafrost regions the circumpolar arctic (Larouche et al., 2015), as well as studies conducted in permafrost-free boreal peatlands (Olefeldt et al., 2013b). Wildfires may burn off above ground vegetation (Zoltai, 1998), which causes a loss in aliphatic C compounds associated with fresh plant material (Olefeldt et al., 2013b), reducing the production and subsequent downward leaching of labile carbon. Additionally, wildfire produces and enriches burned peatlands with ash and char (Flannigan et al., 2008; Olefeldt et al., 2013a). A form of carbon produced due to the impartial combustion of organic matter, char is hydrophobic, dark, and highly aromatic (Flannigan et al., 2008; Olefeldt et al., 2013a; Preston and Schmidt, 2006). It is likely that these mechanisms worked in conjunction with one another to contribute to increased DOC aromaticity and associated decreased BDOC after a wildfire, particularly during the spring. However, the effect of wildfire on DOC composition was not observed during the summer or fall (Figures 4b and 4c). Most lateral movement of water occurs at or just below the water table (Olefeldt et al., 2013a), and in the summer and fall the water table on the peat plateaus existed > 10 cm below the surface (see methods). Peatland wildfires typically only burn the upper 10 – 20 cm of peat (Turetsky et al., 2014), and therefore any effect of burning on DOC composition likely dissipated above the water table in the later seasons.

Permafrost thaw (YB) resulted in enhanced DOC biodegradability when compared to intact peat plateaus, mature bogs, and burned peat plateaus (Figure 5). Biodegradability was also enhanced at BE, yet this was muted by the effect of wildfire, and therefore BDOC at BE was significantly lower than BDOC at YB (Figure 5). Permafrost thaw causes inundation, and biologically labile compounds are protected from decomposition due to anaerobic conditions. Additionally, non-vascular *Sphagnum riparium* mosses produce less aromatic compounds than DOC originating from upland forests or treed peat plateaus (Spencer et al., 2008; Broder et al., 2017), which likely accounts for higher lability observed at young thermokarst bogs. *Sphagnum riparium* dominated thermokarst typically exists on the landscape for up to 100 years until shifts in vegetative composition indicate it has transitioned into mature bogs (Camill, 2005), characterized by *Sphagnum fuscum* (Table 2-1). Once this shift occurs, the effect of permafrost thaw on biodegradability disappears: Mature bog BDOC is similar to P BDOC (Figure 5). Both *Sphagnum fuscum* and *Sphagnum riparium* are characterized by a lack of lignin (Spencer et al., 2008), yet *Sphagnum riparium* contains a higher proportion of non-structural carbohydrates than *Spaghnum fuscum*, which are derived from recent photosynthesis (Turetsky et al., 2008). This likely renders DOC derived from young thermokarst bog-dominated *Sphagnum riparium* more biodegradable than mature bog DOC. Additionally, the water table at MB consistently exists below the surface, and therefore DOC reaching the water table is likely already quite decomposed, compared to young thermokarst bogs (YB, BE), where the water table can exist above the vegetation (Table 2-1). However, enhanced biodegradability off thermokarst bogs was not observed in the summer or fall incubations (Figure 2-5). Higher temperatures in summer and fall when compared to spring (see methods) may enhance microbial activity, and thus the labile DOC leached is likely also rapidly decomposed, reducing the available pool of biodegradable DOC on thermokarst wetlands.

Thermokarst wetlands (YB, BE) produced porewater DOC of greater biodegradability during the spring, and DOC was found in YB porewater in concentrations 1.5 to 3 times higher in the spring and summer than at any other sampling location (Figure 2-4a). With warming temperatures and enhanced wildfire frequency, we are observing the production of more thermokarst wetlands (Vonk et al., 2015; Larouche et al., 2015; Tarnocai et al., 2009), and with that comes the enhanced downstream export of biodegradable carbon (Selvam et al., 2017). If a similar volume of runoff is generated off of both a plateau and young thermokarst bog, the young thermokarst bog will likely produce ~ 6 times more biodegradable DOC than the plateau. Thus, while recent thermokarst only covers approximately 10 % of peatland complexes in the region, these landscape features may dominate the influence on DOC exported from peatlands in terms of biodegradability and ecosystem function in downstream systems. In snowmelt-dominated systems such as the Taiga Plains, the majority of runoff, and thus DOC export, occurs during the spring freshet (Quinton et al., 2009). In fact, prior to our spring sampling period, which occurred towards the end of the spring freshet, 67 % of annual runoff had already occurred (Figure 2-3). Therefore, while the effects on DOC biodegradability from disturbances were only present during spring, these shifts in DOC composition may have important implications for downstream ecosystems given the high hydrological connectivity during this period. While there were no summer storms observed in 2016, historical data shows large inter-annual variability in runoff production (Figure 2-3). Because they enhance hydrologic connectivity (Quinton et al., 2009; Clark et al., 2007), we would likely see a pulse export of aromatic, non-biodegradable DOC directly following summer storm events.

2.4.3 Importance of SUVA and C/N for predicting biodegradability

In the spring, when BDOC was greatest, we observed a strong and significant negative correlation between BDOC and C/N (Figure 2-6a). Significantly lower C/N has been found in fresh extracts, when compared to C/N in peat or litter extracts (Pinsonneault et al., 2016); we found lowest C/N in YB, where *Sphagnum riparium* is dominant (Table 2-1). Similar studies have shown a positive correlation between C/N and degree of source material decomposition, which correlates to lower BDOC (Pinsonneault et al., 2016; Fellman et al., 2008). While there was no relationship observed between BDOC and C/N in the summer or fall, BDOC was < 10 % when C/N exceeded ~45 (Figure 2-6a), suggesting this may be a threshold value, after which carbon has very limited biodegradability. Additionally, increasing C/N typically correlates to higher aromatic C content (Fellman et al., 2008), and therefore SUVA is also a strong predictor of BDOC.

Also in the spring, we observed a significant negative correlation between BDOC and SUVA (Figure 2-6b). In studies that have compared the correlation between BDOC and SUVA similar results have been found (Pissonneault et al., 2016; Larouche et al., 2015; Abbott et al., 2014; Mann et al., 2012; Fellman et al., 2008). High SUVA values correspond to greater aromaticity (Weishaar et al., 2003). Thus, higher values for either of these indices represents microbially recalcitrant DOC, and subsequently reduced BDOC is expected. It appears that in permafrost peatlands in the discontinuous permafrost zone, SUVA may play an especially important role in controlling BDOC: when SUVA values exceeded 3.2 L mg C^{-1} m^{-1}, BDOC was negligible (Figure 6a). Short incubation studies (11 days) conducted on burned boreal peatlands observed high biodegradability (10-20%) even when SUVA exceeded 3 L mg C^{-1} m^{-1} (Olefeldt et al., 2013b), and longer studies (40 days) on thawed permafrost in upland landscape (Larouche et al., 2015; Abbott et al., 2014), observed no real impact of high SUVA on BDOC. However, these studies utilized either soil leachates (Olefeldt et al., 2013b), or stream outflows (Larouche et al., 2015; Abbott et al., 2014), suggesting the relationship between SUVA and BDOC may be dependent on DOC source.

2.4.4 Influence of disturbances and season on photochemical DOC degradation

The penetration of UV radiation in the water column is a function of DOC concentration and composition (Waisar and Robarts, 2004), and aromatic (humic) substances are responsible for absorbing this radiation (Corin et al., 1996). However, there is variability in aromaticity in humic acids (Haumaier and Zech, 1995) – lignin and char may exhibit different light-absorbing properties. By normalizing our samples to similar absorbance, we accounted for differences in optical properties and % aromatics from different sources. Additionally, in small peatland lakes or ponds, most UV light is absorbed in the top 5-50 cm (Laurion and Mladenov, 2013), depending on DOC concentration, thus all our samples were exposed to and absorbed the same amount of UV-light. Therefore, any difference in photochemical DOC loss between sources is attributed to composition only. Recent studies indicate that thermokarst C is particularly photolabile (Selvam et al., 2017), while wildfire may reduce DOC photolability (Haumeier and Zech, 1995; Ward and Cory, 2016). However, we observed no significant differences between sites in either the summer or fall (see results), despite variability in aromatic compounds suggested by differences in SUVA (Figure 2-4b), and there was also no significant relationship between SUVA or C/N and light-dark losses ($p > 0.05$). Therefore, disturbance is likely not a first-order control on photochemical processing in catchments with permafrost peatlands in the discontinuous permafrost zone. However, wildfire can deepen the active layer (Flannigan et al., 2008), and potentially make a large pool of both humified and charred DOC compounds available for downstream export. Therefore, while there was no effect of wildfire on DOC photolability, photodegradation may play an important role in downstream ecosystems draining burned peat plateaus, as aromatic DOC could be exported in large quantities. There was also a significant difference in photolability between summer and fall, when all sites were pooled (Figure 2-7). In the summer, due to longer daylight hours, light treatment samples were exposed to double the amount of incoming PAR when compared to the fall (see methods). Therefore all samples absorbed more light in the summer, which resulted in greater DOC loss when compared to the fall.

There is currently a lack of scientific consensus regarding the role and importance of the two dominant degradation processes in pond carbon cycling (Laurion and Mladenov, 2013; Cory et al., 2015; Vonk et al., 2015; Roiha et al., 2016; Selvam et al., 2017). We observed a significant increase in DOC lost in light treatments relative to the dark treatments during the summer (Figure 2-7, Table 2-3), suggesting photochemical degradation may be an important pathway for DOC transformation in northern ecosystems. This is of particular importance in shallow peatland lakes, where most DOC losses occur through photochemical and UV-mediated microbial degradation (Olefeldt et al., 2013b). However, climate models predict increasing summer cloud cover under a doubling of atmospheric carbon dioxide concentration, which will reduce the amount of shortwave radiation reaching the Earth's surface (Holland and Bitz, 2003), potentially diminishing the importance of photochemical degradation on aquatic carbon cycling in northern peatlands.

2.5 Conclusion

We show that permafrost thaw enhances BDOC in the spring, while wildfire has the opposite effect. This is likely to affect lake carbon cycling and habitat conditions. However, young thermokarst bogs only cover a small fraction of peatland complexes, while peat plateaus typically cover > 50 % of the landscape. Therefore, while permafrost thaw has a stronger impact on BDOC, wildfire may have a more pronounced effect at the catchment scale. Despite the fact the effect of disturbance was only observed in the spring, this is when the catchment is nearly completely hydrologically connected and when the majority of annual DOC is exported.

In a warming world, we can expect increasing rates of thermokarst and more wildfire, suggesting that we can expect large shifts in the composition and magnitude of DOC exported from boreal regions with discontinuous permafrost, although predicting wildfire occurrence and severity is difficult. Thermokarst bog expansion will occur in all peatland complexes as a result of climate warming, while wildfire will only affect specific peatland complexes each year. Thus, at the landscape scale, perhaps we can expect generally more biodegradable DOC being exported, except from catchments affected by wildfire, where the effect of reduced BDOC on peat plateaus might be more important. At longer timescales, however, as these peatland complexes become fully dominated by mature thermokarst bogs, we might again see reduced biodegradability. Also, because these mature bogs act as fire-breaks on the landscape, the occurrence of disturbance in peatland complexes may become less important with time. With altered precipitation and evapotranspiration, we might expect altered seasonality of runoff generation and timing in terms of when peatlands become hydrologically connected to catchment stream networks. Currently, the snowmelt period dominates catchment export in high-latitudes, yet with shorter winters and smaller snow packs, summer DOC export may become more important. We can also expect longer ice-free seasons in lakes, thus enhancing the importance of photodegradation over microbial degradation. In order to assess the net effect of climate change on likely impacts on downstream DOC composition, export, and overall aquatic carbon cycling, our results highlight an important link between season and disturbance, and their effects on DOC susceptibility to transformation.

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Table 2-1. Characteristics of porewater sampling sites.

Site	Dominant vegetation	Near-surface peat type	Permafrost conditions	Water table position[1]
Unburned plateau	Lichens, labrador tea, black spruce	Sylvic[2]	Active layer depth ~60 cm.	At frost table
Young thermokarst bog	*Sphagnum riparium*, water sedge	*Sphagnum riparium*	Permafrost thawed during last 50 years.	+5 to -10 cm
Mature thermokarst bog	*Sphagnum fuscum*, leather-leaf	*Sphagnum fuscum*	Permafrost thawed >100 years ago.	-5 to -20 cm
Burned edge	Sparse labrador tea, dead black spruce	Sylvic	Fire-induced permafrost thaw during last 3 years.	+5 to – 10 cm
Burned plateau	Sparse labrador tea, dead black spruce	Sylvic	Active layer depth ~100 cm.	At frost table

[1]Positive values indicate water table position above the peat surface. Range indicates variability within site throughout the sampling period between May and September, with wetter conditions in spring and drier in fall.

[2] Peat aggraded under permafrost conditions typically identified by the presence of well-decomposed woody remnants and lichen (Robinson, 2000; Zoltai, 1995).

Table 2-2. Two-factor ANOVA assessing the effects of site (P, YB, MB, BE, P) and season (spring, summer, fall) on BDOC.

	Df	Mean Square	F-Value	*p*
Season	2	547.4	131.76	<0.0001
Site	4	166.8	40.15	<0.0001
Season:Site	8	108.3	26.06	<0.0001
Error	46	4.2		

Table 2-3. A two-way ANOVA of Treatment (Dark, Light) and Season (summer, fall) was conducted, where light losses accounted for microbial and photochemical loss. Losses were significantly greater under light treatment (0.75 ± 0.3 mg C L^{-1}) than under dark treatment (0.34 ± 0.2 mg C L^{-1}), but only in the summer. Site was not included in the two-way ANOVA because we observed no significant difference in DOC lost among any sites in either season (one-way ANOVA, $p > 0.05$).

	Df	**Mean Square Error**	**F-Value**	***p***
Season	1	0.0379	2.63	0.125
Treatment	1	1.1211	77.61	<0.0001
Season:Treatment	1	0.062	4.311	0.054
Error	16	0.0144		

Table S2-1 Absolute DOC losses attributed to microbial and photochemical degradation. Microbial losses are determined by losses under dark treatment, while photochemical losses are determined as the difference between losses under light and dark treatments, expressed as the average of all light losses and average of all dark losses. There was no measure of photochemical degradation in the spring, so all losses were attributed to microbial degradation.

Site	Season	Dark loss (mg C L^{-1})	Light loss (mg C L^{-1})	Light – dark (mg C L^{-1})
Peat Plateau				
	Spring	1.47 (0.33)		
	Summer	0.38 (0.07)	0.73 (0.34)	0.35
	Fall	0.31 (0.19)	0.71 (0.14)	0.40
Young Thermokarst Bog				
	Spring	4.89 (0.19)		
	Summer	0.27 (0.34)	0.81 (0.09)	0.66
	Fall	0.46 (0.21)	0.69 (0.16)	0.37
Mature Thermokarst Bog				
	Spring	0.49 (0.18)		
	Summer	0.29 (0.29)	0.80 (0.42)	0.51
	Fall	0.49 (0.20)	0.90 (0.32)	0.42
Burned Peat Plateau Edge				
	Spring	1.81 (0.44)		
	Summer	0.22 (0.22)	0.59 (0.59)	0.37
	Fall	0.56 (0.18)	0.83 (0.25)	0.26
Burned Peat Plateau				
	Spring	0.80 (0.19)		
	Summer	0.27 (0.34)	1.00 (0.26)	0.73
	Fall	0.46 (0.21)	0.58 (0.12)	0.12

Table S2-2 Correlation of ion concentrations of peat porewater and biodegradability by season based on linear regressions. Significance (p<0.05) indicated by *. Correlations between various ions and BDOC were strongest in the spring and there were no significant correlations in either the summer or fall.

	Ion	R^2	p
Spring			
	TDP	**0.81**	**0.036***
	Cl^-	0.44	0.13
	SO_4^{2-}	0.15	0.52
	Al^{3+}	0.10	0.59
	Na^+	0.099	0.61
	K^+	0.68	0.09
	Ca^{2+}	0.53	0.1
	Mg^{2+}	0.70	0.077
	$Fe^{2+/3+}$	0.47	0.20
Summer			
	TDP	0.39	0.26
	Cl^-	0.74	0.06
	SO_4^{2-}	0.36	0.29
	Al^{3+}	0.40	0.25
	Na^+	0.20	0.44
	K^+	0.32	0.32
	Ca^{2+}	0.038	0.75
	Mg^{2+}	0.076	0.65
	$Fe^{2+/3+}$	0.16	0.50
Fall			
	TDP	0.2	0.45
	Cl^-	0.04	0.74
	SO_4^{2-}	0.06	0.84
	Al^{3+}	0.26	0.38
	Na^+	0.43	0.23
	K^+	0.10	0.60
	Ca^{2+}	0.0090	0.88
	Mg^{2+}	0.42	0.23
	$Fe^{2+/3+}$	0.066	0.68

Table S2-3. Least-square mean results from a two-way ANOVA.

Site	Season	BDOC (%) LSMEAN	LSMEAN Number
Plateau	Spring	9.53	1
Plateau	Summer	3.94	2
Plateau	Fall	4.62	3
Young Thermokarst Bog	Spring	25.6	4
Young Thermokarst Bog	Summer	2.11	5
Young Thermokarst Bog	Fall	4.2	6
Mature Bog	Spring	3.34	7
Mature Bog	Summer	3.94	8
Mature Bog	Fall	2.93	9
Burned Edge	Spring	14	10
Burned Edge	Summer	2.14	11
Burned Edge	Fall	4.87	12
Burned Plateau	Spring	5.48	13
Burned Plateau	Summer	1.13	14
Burned Plateau	Fall	3.67	15

Table S2-4. Bolded LSMEAN Number from Table S3 signifies significant differences between site and season (* = p<0.001).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
2	**0.049**													
3	0.077	1.00												
4	*	*	*											
5	**0.0016**	0.99	0.95	*										
6	**0.037**	1.00	1.00	*	0.98									
7	**0.0034**	1.00	0.99	*	0.99	0.99								
8	**0.0047**	0.99	0.99	*	1.0	0.99	1.00							
9	**0.0013**	0.99	0.99	*	0.99	0.99	1.00	1.00						
10	0.106	*	*	*	*	*	*	*	*					
11	*	0.99	0.88	*	1.0	0.99	0.99	1.0	0.99	*				
12	0.077	1.0	0.99	*	0.86	0.99	0.99	0.97	0.97	*	0.72			
13	0.28	0.99	0.99	*	0.69	0.99	0.96	0.87	0.99	*	0.50	0.45		
14	**0.002**	0.92	0.63	*	0.99	0.80	0.97	0.99	0.86	*	0.99	1.00	0.29	
15	**0.03**	1.0	0.99	*	0.99	1.00	1.0	0.99	0.99	*	0.99	0.99	0.99	0.96

Table S2-5. Water chemistry parameters measured at three porewater locations within each of the five sites, with standard deviation in brackets.

	P	YB	MB	BE	BP
EC (µS cm^{-1})	55.70 (5.95)	57.50 (0.94)	61.93 (4.19)	38.53 (1.70)	51.33 (4.91)
pH	3.80 (0.32)	4.13 (0.10)	4.05 (0.32)	3.76 (0.18)	4.20 (0.38)

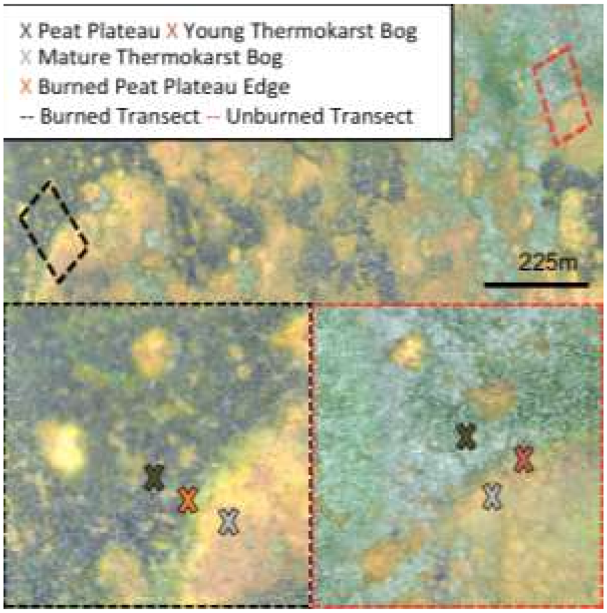

Figure 2-1. Transects and sample sites in a recently burned and unburned area of the studied peatland complex in the Northwest Territories of Canada (61.20 N, 120.08 W). The peatland complex encompasses both permafrost (peat plateau) and expanding non-permafrost (thermokarst bogs) ecosystems. A 2013 wildfire partially affected the peat plateaus, which by 2016 had led to substantial additional permafrost thaw along the burned peat plateau edges. Aerial photo source: William Quinton, 2016.

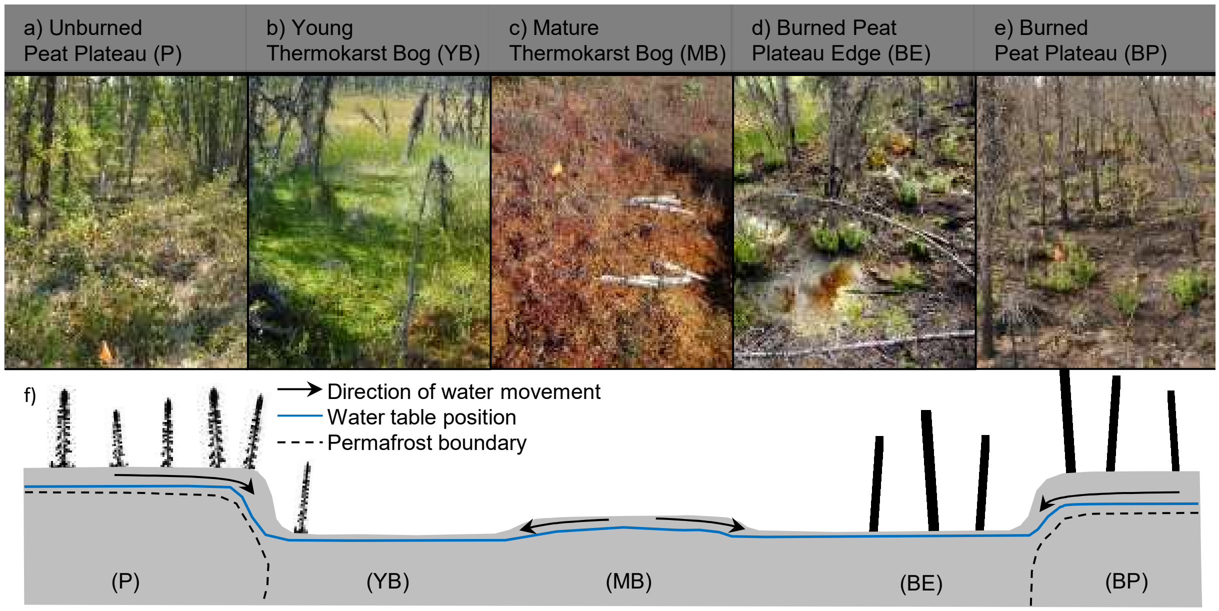

Figure 2-2. Representative photos of sites for porewater collection; (a) unburned peat plateau, (b) young thermokarst bog (c) mature thermokarst bog, (d) burned peat plateau edge, and (e) burned plateau. The burned sites were affected by wildfire in 2013, three years prior to the study. Within each site, porewater was collected from three locations and pooled immediately. Water flows off the plateaus and bogs into the subsided thermokarst where it can move downstream.

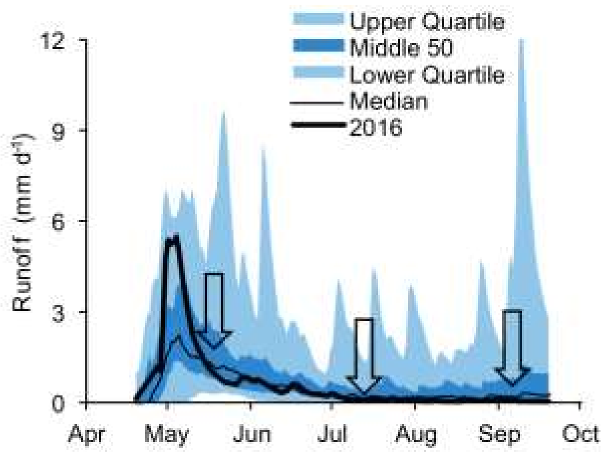

Figure 2-3. Timing of peatland porewater collection in 2016 contrasted with the hydrological runoff regime of a nearby peatland-rich catchment. The three sampling events are indicated by arrows. Discharge from Scotty Creek outlet (61.42 ˚N, 121.46 °W) located 60 km west of the studied peatland is used as an example to show the hydrological regime of peatland–rich catchments in the region. Discharge data compares the period from 1995-2015, showing the historical inter quartile range, top quartile, and bottom quartile, with the 2016 data. Discharge data from Environment Canada (https://wateroffice.ec.gc.ca/)

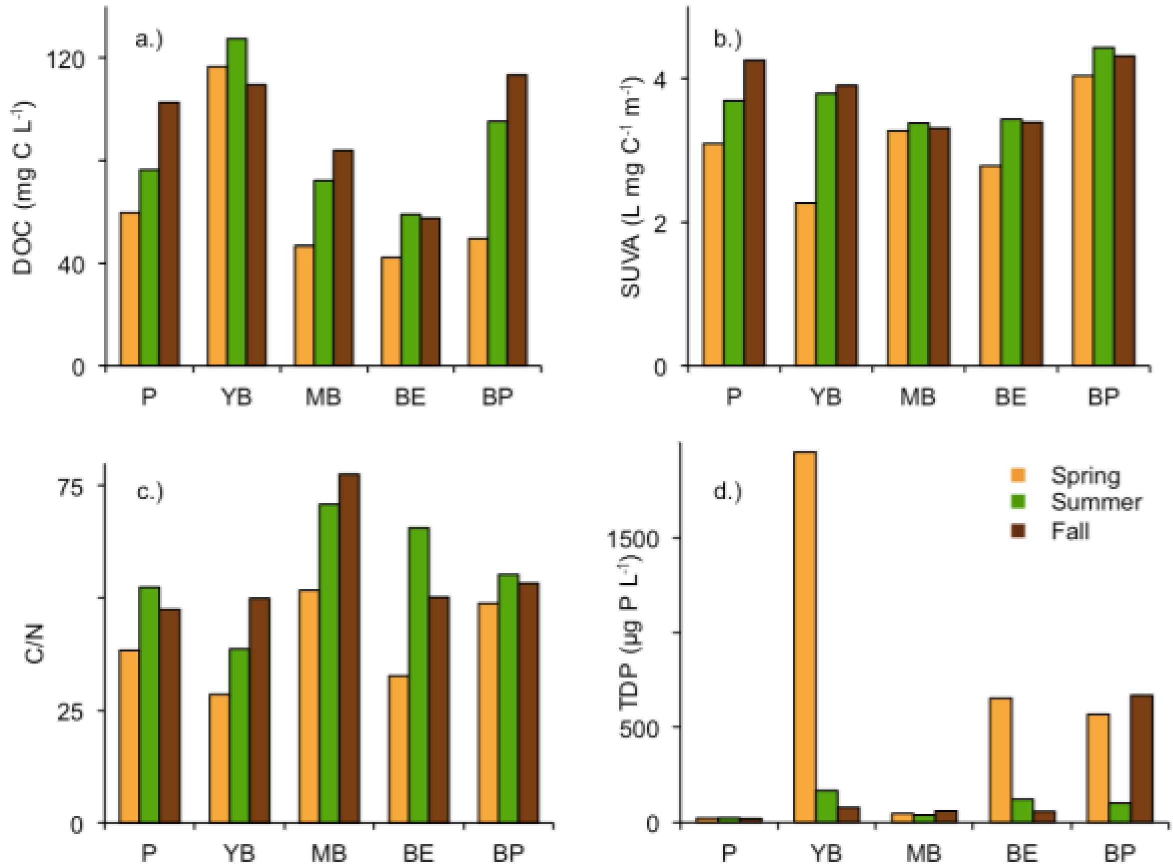

Figure 2-4. Seasonal variability of undiluted peatland porewater chemistry in investigated sites: a.) dissolved organic carbon concentration (mg C L^{-1}), b.) specific ultraviolet absorbance (SUVA, L mg C^{-1} m^{-1}), c.) carbon to nitrogen ratio (mol : mol), and d.) total dissolved phosphorus concentration (µg P L^{-1}), as influenced by permafrost conditions and recent wildfire or thaw disturbances. Values come from porewater samples collected from the MacroRhizons, after being pooled, prior to being diluted and inoculated for incubation.

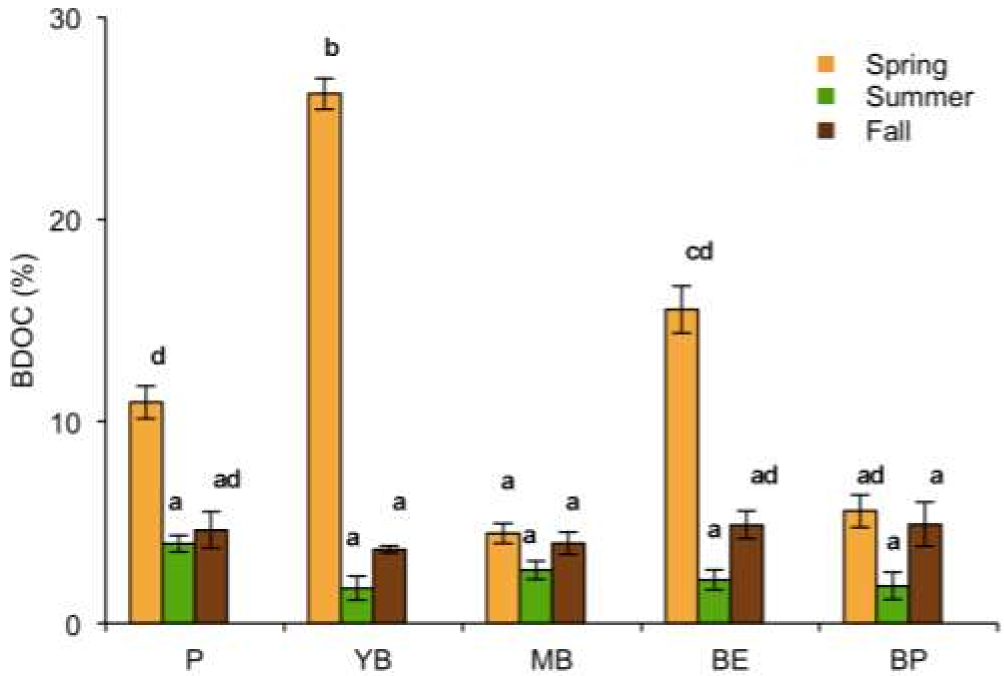

Figure 2-5. Seasonal influence on DOC biodegradability (BDOC) between sites, as assessed by 7-day dark incubations, of porewater collected in sites with varying permafrost conditions and recent disturbance histories. Error bars represent one standard error (n = 5). Results from a two-way ANOVA for assessing differences in BDOC among season, site, and their interaction is signified with lower case letters, where different letters correspond to significant differences, and are also reported in Table 2-2.

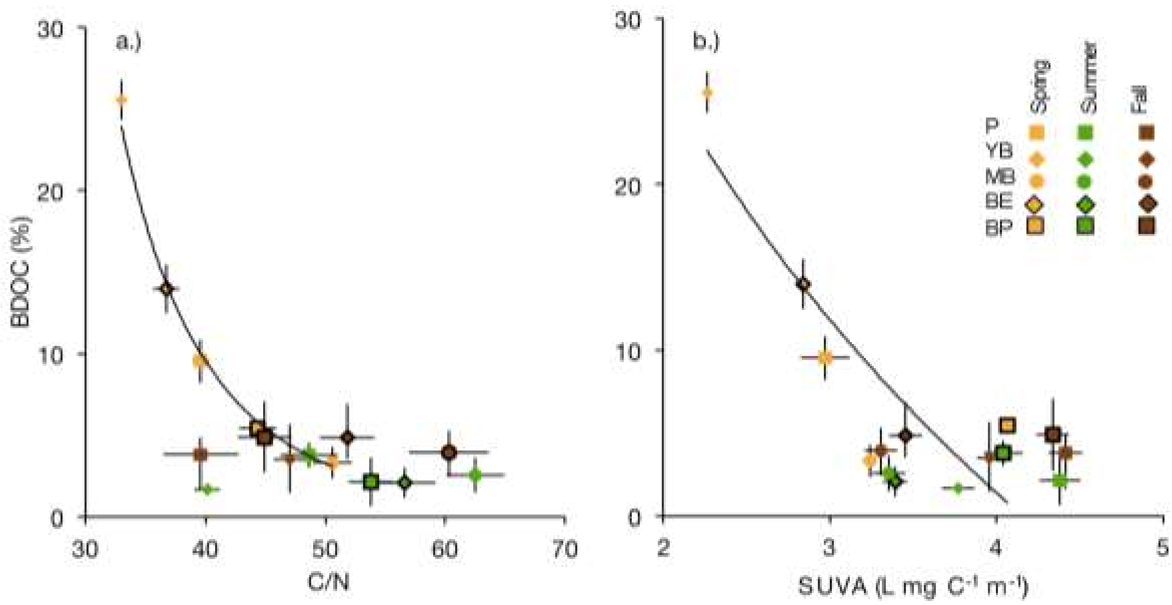

Figure 2-6. Relation between BDOC and a.) C/N and b.) SUVA. Permafrost thaw caused shifts in DOC composition that resulted in decreased biodegradability, while wildfire had the opposite effect. The significant correlation between BDOC and a) C/N and b) SUVA was only observed in the spring.

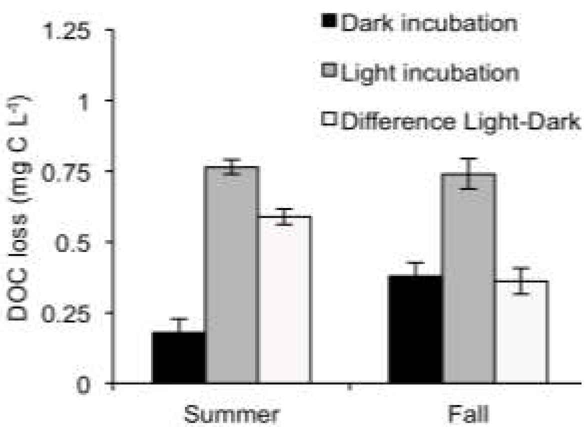

Figure 2-7. Average absolute DOC loss (mg C L^{-1}) among all sites (n = 5) for summer and fall incubations under both dark and light incubation conditions. The difference between losses under light and dark treatments is attributed to photodegradation (photolosses). Error bars represent one standard error.

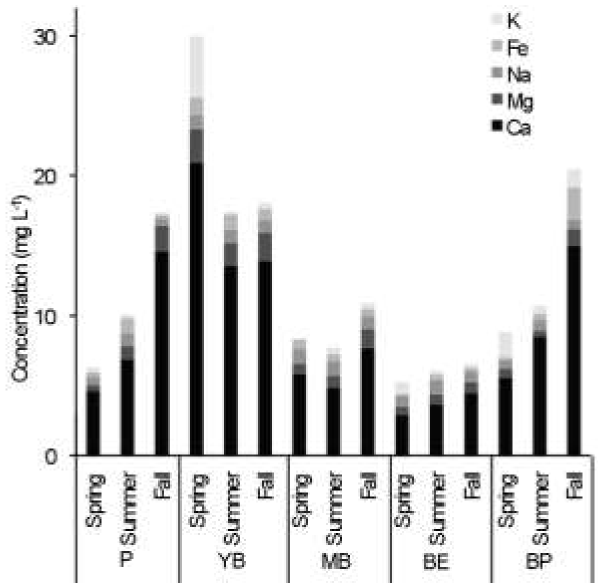

Figure S2-1. Seasonal variability of major cation concentrations among sites. Samples represent a pooled sample from 3 plots at each site, see methods.

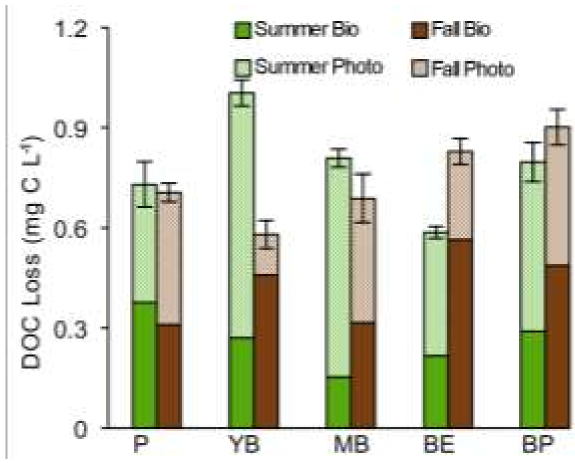

Figure S2-2. Site and treatment specific absolute DOC loss in summer and fall. Overall losses were similar between seasons, but light losses were more important in the summer, while dark losses were more important in the fall. There was no significant difference (p>0.05) between sites in summer or fall, but a significant difference between light and dark losses in the summer was found.

Chapter 3: Importance of spring freshet for magnitude and chemical composition of dissolved organic carbon exported from burned and unburned peatland-rich catchments within the discontinuous permafrost zone.

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Abstract

Export of DOC represents a key component of the carbon balance of many terrestrial ecosystems, and furthermore regulates the carbon balance of downstream acquaic ecosystems. The spring freshet is an often-understudied period for catchments within the permafrost region, but represents a vital period of the year for our understanding of annual DOC export. Both climate change and disturbances, such as wildfire, have the potential to alter the magnitude and chemical composition of catchment DOC expot by affecting either the DOC characteristics or runoff generation of available water sources. In this study we monitored water chemistry, runoff, and DOC chemical composition at the outlets of a 321 km^2 recently burned catchment and a 152 km^2 undisturbed catchment in the peatland-rich Taiga Plains of boreal western Canada from early spring until fall. The two catchments had very similar timing, overall magnitude, and chemical composition of their DOC export. Any effect of wildfire appeared limited to increased DOC export during the low-flow summer periods. Total DOC export in 2016 was in the range from 1.4 – 2.0 g C m^2, with the four week spring freshet period (April 29 – May 26) responsible for ~ 65 % of annual DOC export. Periods of higher runoff were associated with lower DOC concentrations but higher DOC aromaticity and average molecular weight. These shifts in DOC characteristics were consistent with shifts in the relative contribution to runoff from organic soil porewater, mineral soil groundwater, and precipitation water. However the ~ 8 day period during early spring, which was responsible for ~ 25 % of annual DOC export, exported DOC with distinctly high aromaticity and molecular weight. Our results suggest that DOC export from peatland rich catchments in the permafrost region, in terms of both quantity and quality, is more sensitive to climate change through impacts on runoff generation than through altered fire regimes

3.1 Introduction

Northern high-latitude regions transport more than 100 Tg dissolved organic carbon (DOC) from terrestrial ecosystems to the Arctic Ocean annually (Holmes et al., 2012), yet roughly twice as much DOC is believed to enter inland aquatic ecosystems as is exported to the ocean (Cole et al., 2007). Losses of terrestrial DOC during transit in rivers and lakes result from microbial and photochemical processes that cause mineralization into greenhouse gases or burial into sediments at rates that are regulated by DOC concentration and chemical composition (Sobek et al., 2003; Cory and Kaplan 2012; von Wachenfeldt et al., 2009). Peatlands are major sources of DOC to inland waters at high latitudes, and dominate DOC export and its chemical composition when catchment peatland coverage exceeds 10% (Agren et al., 2008) Altered peatland DOC export arising from ongoing climate change may have cascading effects on both aquatic carbon cycling and the carbon balance at the landscape level (Lundin et al., 2016). The brief spring freshet period dominates annual runoff from many high-latitude catchments (Quinton et al., 2009) and is thus crucial for understanding controls on catchment DOC export and its chemical composition – yet this period is often understudied within the permafrost region due to practical difficulties in achieving high frequency sampling.

Chemical composition of DOC varies among catchment DOC sources, and is believed to strongly influence its downstream fate. All natural samples of DOC include a wide mix of different molecules (Wright and Reddy, 2009), which makes determining specific chemical composition impossible. However, optical properties of DOC can be used to resolve bulk characteristics of a DOC sample; the specific-UV absorbance (SUVA) at 254 nm, relative to DOC concentration, is linked to aromaticity (Weishaar et al., 2003), and the slope of absorbance between 275-295 nm is inversely linked to average molecular size (Fichot and Benner, 2012). These two indices are often negatively correlated (Broder et al., 2017). In boreal catchments, near-surface organic soils in peatlands and riparian zones of upland forests contribute terrestrial DOC into freshwater systems (Carey, 2003; Ågren et al., 2008; Ledesma et al., 2017). Among DOC compounds sourced from organic soil there exists high variability in chemical composition: plateau porewater can be 1.5 times as aromatic as thermokarst wetlands (Chapter 2) and within the organic soil horizon, aromaticity increases at depth (Ågren et al., 2008; Olefeldt et al., 2013a), reflecting higher rates of decomposition and humification (Hugelius et al., 2012). In mineral soils, DOC is made up of microbially derived compounds not easily decomposable due to its exposure to fractional sorption, co-precipitation, and mineral processing as it travels downward (Kaiser and Kalbitz, 2012). Shifts between upland and peatland dominated catchments in the boreal forest create differences in DOC sources, which in turn affect downstream DOC export by altering DOC chemical composition.

Although boreal catchment export of DOC varies spatially between catchments depending on relative abundance of peatlands and uplands, DOC export characteristics likely vary temporally depending on hydrological connectivity of different DOC sources. Peatland complexes in the discontinuous permafrost zone of western Canada are a mosaic of upland forests, permafrost peat plateaus, and permafrost-free channel fens and bogs: the former two are runoff generators, bogs can be connected or isolated, depending on catchment connectivity, and fens convey this runoff downstream (Quinton et al., 2009; Wieder and Vitt, 2010). During the spring freshet the catchment is hydrologically well connected (Quinton et al., 2009), and streamflow is dominated by near-surface DOC sources, which contain labile DOC compounds due to preservation during cold winter months (Fellman et al., 2009). During periods of low flow, bogs may become hydrologically isolated (Quinton et al., 2009), and water originates predominantly from subsurface flow paths exporting deeper mineral soil DOC (Olefeldt and Roulet, 2014). Despite its importance, there exist limited high-frequency data on DOC flux and export during the spring period (Tunaley et al., 2016; Finlay et al., 2006); if high frequency sampling is not focused on short-lived yet high-flow periods such as the freshet, it is likely that any conclusions drawn could be inaccurate.

Climate change may also impact DOC dynamics, and, globally, northern Canada's climate is warming faster than anywhere else (Johannessen et al., 2004). Runoff is a major flux of water out of terrestrial ecosystems (Bring et al., 2016) and increasing atmospheric moisture coupled with the reactivation of subsurface groundwater flow paths have been linked to increased runoff from northern catchments (Manabe et al., 2004; St. Jacques and Sauchyn, 2009). The continental boreal forest is the most vulnerable region to changing wildfire regimes (Tarnocai, 2009; Zoltai et al., 1998). Wildfire can burn the upper soil organic layer (Flannigan et al., 2008) and produce aromatic carbon compounds (Preston and Schmidt, 2006). Increased DOC aromaticity and decreased biodegradability in peatland porewater after a fire has been recorded on both the Boreal and Taiga Plains (Olefeldt et al., 2013b; Chapter 2). Wildfire can remove surface vegetation, reduce evapotranspiration, and increase soil temperature, which may thicken the seasonally thawed layer (Flannigan et al., 2008, Zoltai et al., 1998). It remains unclear whether shifting runoff pattern or enhanced wildfire frequency has a greater impact on the composition of exported DOC reaching downstream ecosystems.

We utilized high frequency data collection to monitor DOC characteristics during the traditionally under-sampled spring freshet period. The objective of this study was to better capture DOC dynamics during the spring freshet, while determining if the effect of wildfire on DOC characteristics at the catchment outlet is consistent with the effect of wildfire on peatland porewater DOC composition. With a warming climate, wildfire is expected to have a more pronounced effect on northern ecosystems, and altered DOC export throughout the catchment may have implications for the function of downstream ecosystems or carbon cycling at the landscape scale.

3.2 Methods

3.2.1 Catchment descriptions

Scotty Creek (SC) and Notawohka Creek (NW) drain two catchments located in the discontinuous permafrost zone of Canada's western boreal forest (Figure 3-1). The SC outflow at the Liard Highway (61°24 W, 121°26 N) has a 152 km^2 catchment that has not been affected by any major fires in the last 50 years. The NW outflow at the Mackenzie Highway (61°08 W, 120°17 N) has a 321 km^2 catchment that was 94% burned in 2013 (Northwest Territories 2013 Fire Scar Map). Both catchments are located in the Taiga Plains Mid-Boreal Ecoregion within the Mackenzie Basin (Ecosystem Classification Group, 2007), characterized by short summers and long, dry winters (Quinton et al., 2009). Mean annual temperature is ~ -3.5 °C and mean annual precipitation is ~350 mm with the majority falling as snow (Ecosystem Classification Group, 2007; Quinton et al., 2009; Meteorological Services of Canada, 2002). The bedrock of the catchments is dominated by sedimentary shale, limestone, and dolomite rocks formed during the Devonian period (Wheeler et al., 1996), while surface geology is dominated by thin to thick tills and glaciolacustrine silt and clay deposits formed during glacial retreat after the last glacial maximum (Aylsworth et al., 2000). Both catchments are level to gently undulating with < 50 m difference between outflow and maximum elevation (248 - 295 m and 263 - 300 m above sea level for SC and NW, respectively). The ecoregion is co-dominated by mixed-wood (trembling aspen, white spruce) forests in well-drained locations and extensive lowland peatlands, where peat deposits can be up to 8 m thick (Quinton et al., 2009). The peatlands are a mosaic of permafrost peat plateaus, permafrost-free thermokarst bogs and channel fens, and shallow lakes (Wieder and Vitt, 2010; Quinton et al., 2009). Peat plateaus are dominated by black spruce (*Picea mariana)*, Labrador tea (*Rhododendron groenlandicum*), and a variety of lichen species; thermokarst bogs support *Sphagnum* spp and low shrubs, channel fens vary from being open canopy to dominated by shrubs mostly from the *Betula* genus (Wieder and Vitt, 2010; Quinton et al., 2009).

We used digital elevation models and satellite image interpretation to delineate the stream networks and catchment limits. A supervised classification (ArcGIS 2017, ESRI, Redlands, CA, USA) of SC and NW catchments' land cover was carried out using publicly available MODIS satellite imagery taken before the 2013 fire (zoom earth, NASA, USA). Easily distinguished differences of spectral signatures were utilized to separate four land cover classes: 1) open water, 2) upland mixed-wood forests, 3) channel fens, and 4) peat plateau and thermokarst bog complexes (Figure 3-2). Image resolution was too poor to further separate peat plateaus and thermokarst bogs. The two catchments had similar proportional contributions from different land cover classes; both dominated by peat plateau and thermokarst bog complexes. The NW catchment had a higher proportion of open water, with much of the catchment runoff passing through a set of lakes.

3.2.2 Catchment discharge and runoff

Air pressure and pressure at the bottom of the water column were continuously monitored at one-hour intervals with HOBO Pressure Loggers (Onset, Bourne, MA, USA) from 04-29-2016 to 09-09-206 at SC and NW catchments. Water stage was calculated as the difference between water pressure and air pressure assuming a 1 kPa increase in pressure difference corresponds to a 10 cm rise of the water table, and was verified by taking stage measurements at a stationary staff gauge throughout the ice-free season. A rating curve for Notawohka for estimating continuous discharge was based on seven manual sampling occasions of water flow velocity over the ice-free season (SonTek Flowtracker Handheld ADV, San Dieo, CA, USA). Discharge was estimated by multiplying stream velocity at 40 % depth by cross-sectional area at 10 locations along a transect spanning the width of the stream, known as the velocity-area method for estimating discharge (Shaw, 1994). Using the rating curve and the hourly record of stream stage we calculated an hourly discharge record for the entire growing season. The Water survey of Canada has monitored discharge at SC since 1995 (wateroffice.ec.gc.ca), and we also collected water flow velocity data at SC on seven occasions from early spring thru fall. Runoff was estimated by dividing daily discharge interpolations by catchment area.

3.2.3 Catchment outflow water sampling and analysis

We collected grab samples on sixteen occasions over the growing season to analyze for DOC concentration and absorbance properties. The data from grab samples were also used to calibrate hourly data collected by a spectrophotometer (see below). At the time of water sampling, we filtered two replicates of 70 mL through glass fiber filters with a 0.7 µm nominal pore size (Grade GF/F, Whatman) – 60 mL of the filtered sample was placed in a glass amber bottle. Amber bottles were acidified with 0.6 mL 2 N HCl^- to reduce pH to < 2 and thus prevent further microbial activity during transport to the laboratory. The remaining 10 mL of filtered sample, and another 10 mL of unfiltered sample were each transferred into a 1 cm path-length quartz cuvette for determination in the field of UV-vis absorbance between 230 - 600 nm using a portable spectrophotometer (Flame-DA-CUV-UV-VIS light source and Flame-S Spectrophotometer, Ocean Optics, Dunedin, FL, US). Within eight days of sample collection, acidified samples were analyzed for DOC and total dissolved nitrogen (TDN) concentration on a TOC-L combustion analyzer with a TNM-L module; concentration measurements are based on four injections, where the average standard deviation for injections of the same sample was 0.07 mg C L^{-1} and 0.008 mg N L^{-1} (Shimadzu, Kyoto, Japan).

3.2.4 Continuous monitoring of DOC characteristics

We deployed a submersible *in situ* spectrophotometer at each catchment (spectro::lyser, Aquatic Life Limited for s::can, Vienna, Austria) on 04-29-2016 or 04-30-2016. The instrument directly measures absorbance at 2.5 nm intervals from 200 to 700 nm, which can then be used to calculate absorbance-based metrics within the water column; one minute prior to each measurement, an automated brush removed any debris to remove fouling. Measurements were taken continuously at four-hour intervals, but battery malfunction at NW required us to stop monitoring on 08-17-2016. At SC, the spectrophotometer was disturbed due to ice break up at early snowmelt, and was returned to normal functioning on 05-19-2016. However, fouling not alleviated with the automatic cleaning brush caused higher than acceptable absorbance values, which forced us to discard SC spectrophotometer data after 06-21-2016. HOBO Freshwater conductivity loggers (Onset, Boruner, MA, USA) were deployed on the same day as the spectrophotometer, and electrical conductivity (EC, µS cm^{-1}) was monitored on one hour intervals at both catchments.

3.2.5 Utilizing tracers to determine seasonal changes in contributors to runoff

We assumed three catchment water sources as potential runoff end-member components to execute hydrographic separation: organic soil porewater, precipitation, and groundwater. We chose to use absorbance at 254 nm (A_{254}) and EC as two tracers in our streamflow separation because of continuous (EC) or high frequency (A_{254}, sixteen sampling dates from spring to fall) data monitoring and little variation within each water source. Organic soil porewater chemistry was collected at 3 locations within each of an intact permafrost peat plateau, young thermokarst bog, mature thermokarst bog, recently burned edge at the boundary of the thermokarst bog and plateau, and burned peat plateau; pits were dug to the water table and water was collected and filtered to 1.6 µm (Grade GF/F, Whatman) for absorbance measurements, and remained unfiltered for electrical conductivity measurements (YSI Professional Plus Multiparameter Water Quality Instrument, Yellow Springs, Ohio, USA). We did not separate upland sources from peatland influences, but because studies focused on upland soil porewater have found EC < 110 µS cm^{-1} and absorbance > 1.7 m^{-1} (Jantze et al., 2015; Kothawala et al., 2015); the organic soil porewater end-member is assumed to be a mixture of both sources. Precipitation and groundwater were not directly sampled; instead, values published in regional studies were utilized (Hayashi et al., 2004; Fraser et al., 2001). Two tracers allowed us to use the three-component separation model (Eq. 2; Eq. 3) (Christopherson and Hooper, 1992) to determine runoff contributions from each water source as described by Olefeldt and Roulet (2014) (Eq. 1):

$$R_T = R_S + R_G + R_P \ (1)$$

$$C_T^{A254} - C_P^{A254} = R_S \times C_S^{A254} + C_G^{A254} \times R_G + C_P^{A254} \times R_P \ (2)$$

$$C_T^{EC} - C_P^{EC} = R_S \times C_S^{EC} + C_G^{EC} \times R_G + C_P^{EC} \times R_P \ (3)$$

where R_T is the total measured catchment runoff, R_S, R_G, and R_P the runoff contribution from organic soil porewater, groundwater, and precipitation, respectively. C_T^{A254} and C_T^{EC} are the measured A_{254} and EC at each catchment sampling point, and C_S, C_G, and C_P are A_{254} and EC for each component. Some component chemistry was assumed from literature values, and because we have high uncertainty of the component signatures, we also have large uncertainties for the resolved contribution of each component to runoff generation. However, we believe that the assumptions are valid to at least indicate seasonal trends within each catchment.

3.2.6 Indices of DOC chemical composition

The spectral slope coefficient ($S_{275\text{-}295}$), or the slope of log-transformed absorbance between 275 nm and 295 nm (Helms et al., 2008), is a proxy for DOC composition and is inversely related to molecular weight, while being directly related to % terrigenous DOC (Obernosterer and Benner, 2004; Fichot and Benner, 2012). Specific ultraviolet absorbance (L mg C^{-1} m^{-1}) is the absorbance of the water sample at 254 nm normalized to DOC concentration, where higher SUVA values correspond to a greater degree of aromaticity (Weishaar et al., 2003). Grab sample DOC data was used to calculate SUVA at both catchments. Because continuous data is available only at NW, $S_{275\text{-}295}$ is not available for SC.

3.2.7 Estimating DOC export

At NW, we utilized the discharge-stage rating curve to estimate annual runoff, which subsequently was used to estimate DOC export using Method 5 for estimating DOC export (Walling and Webb, 1985; Clark et al., 2007):

$$F = K \cdot Qr \frac{\sum_{i=1}^{n} CiQi}{\sum_{i=1}^{n} Qi} \quad (4)$$

where *F* is the total solute export over a time period, *K* is conversion factor (number of seconds in the time period), Q_r is mean discharge from a continuous record, Q_i is the instantaneous discharge at any given point, C_i is the instantaneous DOC concentration, and *n* is the number of samples. Method 5 (Eq. 4).

Uncertainties in solute export can be estimated when instantaneous measurements are collected at frequencies as low as one week (Littlewood, 1992; Clark et al., 2007); however, because our rating curve has less than one measurement per week. Uncertainty of DOC export can be estimated, but it assumes negligible error and frequent runoff measurements (Littlewood, 1992; Clark et al., 2007). However, our rating curves were poorly constrained, particularly when stage was high. We used the 95 % confidence intervals (CI) of the rating curve to estimate uncertainty of runoff, and assume uncertainty in DOC export is attributed solely to runoff uncertainty.

We utilized the correlation between runoff and DOC concentration in 2016 (R^2 = 0.71, p < 0.005) and historical discharge data collected at SC between 1995-2015 to estimate quantities of, and visualize trends, in DOC export at SC over the last 20 years.

3.3 Results

3.3.1 Discharge and catchment runoff

Discharge at SC was measured by Environment Canada, and a strong correlation with discharge measured using the velocity-area method (R^2 = 0.99) provides confidence in our NW discharge estimates (Figure S3-3). Discharge at NW was estimated based on the rating curve between stage and manual discharge measurements (R^2 = 0.96, Figure S3-4). Issues with ice build-up in the channel during early spring led us to not use the rating curve to estimate discharge, and instead discharge was interpolated linearly between sampling occasions from the onset of continuous data monitoring until May 7. We define early spring as the onset of monitoring (April 29) to peak flow (May 5 and May 8 at SC and NW, respectively) - or the rising limb of the hydrograph - and late spring as the falling limb of the hydrograph to the end of the freshet (May 26). The spring freshet lasted until May 26 in both catchments; here runoff reached a minimum and any increases in runoff after this point can be attributed to rainfall (climate.weather.gc.ca). Peak runoff (4.86 mm d^{-1}) at SC occurred on May 5, while at NW runoff peaked (4.81 mm d^{-1}) on May 8 (Figure 3-4). Total runoff at SC was 92.0 mm, while at NW it was 84.7 mm. After snowmelt, both catchments exhibited baseflow maintained by small summer storms – most or all of which did not generate substantial discharge signals at either catchment outlet (Figure 3-4). Runoff generation exhibited large inter-annual variability over the last 20 years and, when compared to historical trends, 2016 runoff generation at SC was greater during the spring freshet than average, yet, during the summer, was in the lower 25% of runoff between 1995-present (Figure 3-3).

3.3.2 Seasonal trends in water chemistry and DOC characteristics

Water sampling and stream water quality monitoring began prior to complete ice breakup as indicated by near-zero temperatures during the early sampling occasions, and sampling continued until shortly before fall freezeback (Figure 3-4a). Electrical conductivity increased from spring through summer, with minor decreases in EC following small summer storms. Electrical conductivity was greater at NW than at SC for most of the monitoring period (Figure 3-4b) and exhibited a negative logarithmic correlation to runoff (SC: $R^2 = 0.70$, $p < 0.0001$; NW: $R^2 = 0.88$, $p < 0.0001$) (Fig 3-5a). Furthermore EC and runoff exhibited a hysteresis pattern during spring freshet at both catchments, with lower EC during the rising limb of spring freshet than at the receding limb (Figure 3-5a).

Dissolved organic carbon concentration followed a similar trend as EC (Figure 3-4c), with DOC concentrations increasing after the spring freshet. A slight drop in DOC concentration at NW in summer corresponded to a storm, but this was not observed at SC. Similar to EC, DOC concentration was greater at NW than at SC throughout the entire freshet and most of the summer, and at both catchments exhibited a negative logarithmic correlation to runoff (SC: $R^2 = 0.71$, $p = 0.00312$; NW: $R^2 = 0.89$, $p = 0.00125$). Dissolved organic carbon followed similar trends as EC when compared to runoff (Figure 3-5b) and exhibited a hysteresis pattern during spring freshet, with lower DOC concentrations during early spring than expected, based on the relationship to runoff. At both catchments, DOC concentration was positively correlated to EC (Figure S3-3) SC: $R^2 = 0.90$, $p < 0.0001$; NW: $R^2 = 0.88$, $p < 0.0001$). During the freshet, A_{254} at both outlets remained steady at ~ 0.6 m^{-1}, but rapidly increased at the end of the spring freshet (Figure 3-4d). Continuous absorbance data was not available at SC for the entire summer (see methods), but grab samples show A_{254} was lower at SC than NW during the summer (Figure 3-4d).

Since absorbance did not follow the same seasonal trends as DOC concentration, SUVA (mg C L^{-1} m^{-1}) values dropped following spring freshet (Figure 3-4e). SUVA values were consistently higher at SC than at NW during the freshet, but lower absorbance at SC post snowmelt corresponded to lower SUVA values in SC. SUVA was higher during early snowmelt than expected based on the relationship between SUVA and runoff (Figure 3-5c, SC: logarithmic model $R^2 = 0.52$, $p = 0.001521$; NW: linear model $R^2 = 0.25$, $p = 0.02951$). Additionally, higher EC corresponded to lower SUVA (Figure S3-3, SC: $R^2 = 0.75$, $p = 0.0002711$; NW: $R^2 = 0.71$, $p = 0.000611$). Continuous absorbance data was not available for the entire summer (see methods) and thus spectral slope coefficient data is only available in high resolution for NW (Figure 3-4f). There was a rapid increase in $S_{275-295}$ from early to late spring, and values peaked at the end of the freshet (Figure 3-5d, $R^2 = 0.51$, $p < 0.0001$). Once the freshet was over, $S_{275-295}$ decreased to values similar to early snowmelt. There was also a significant relationship between SUVA and $S_{275-295}$ measured at NW (Figure S3-2).

3.3.3 Tracing seasonal trends in changing water sources

Shifts in water chemistry (EC and A_{254}) suggested a gradual shift in runoff from dominance of precipitation water during spring towards a dominance of groundwater during summer. Dissolved organic carbon was sourced only from organic soil porewater during the freshet, and was co-dominated with inputs from groundwater during summer. Both catchments exhibited similar tends in shifting water sources throughout the season, and stayed within the confines of the three identified potential end-member tracers – precipitation, mineral soil groundwater, and organic soil porewater (Figure 6a and b). Large error bars in groundwater EC values account for regional differences in groundwater characteristics published in literature. During early spring, A_{254} and EC at SC were lower than values at NW, but overall this time frame was dominated by contributions peatlands at both catchments. As the freshet progressed, influences from groundwater shifted EC values higher, but absorbance remained stable. After the freshet, snowmelt dilution was minimal and precipitation signals seen only at NW were created mostly by summer storms (Figure 3-3), with the dominant influence coming from groundwater. Organic soil porewater inputs into the system increased slightly after the freshet as well, but generated only about ~ 20 % of the runoff (Figures 3-6c and 3-6d). Due to the large uncertainty in end-member signatures (particularly of EC in groundwater and in A254 in organic soil porewater) error bars represent wide 95% confidence intervals of each end-member contribution to runoff.

3.3.4 DOC export

Total DOC export summed 1.40 g C m^{-2} and 1.89 g C m^{-2} at SC and NW, respectively. Given the uncertainty and lack of multiple sampling dates in our discharge estimates, we cannot provide accurate measures of uncertainty in DOC export, but estimate it to be no more than 30 %. More than half of the annual DOC export (65 % at SC, 59 % at NW) was exported during the spring freshet at both catchments, with early spring accounting for 27 % and 26 % at SC and NW, respectively (Figure 3-7a). Additionally, DOC export plateaued on June 30 at SC, and did not cumulatively exceed ~0.1 mg C m^{-2} for the remainder of the summer. However, at NW, export continued to increase through July into September: approximately 0.5 mg C m^{-2} was exported during this time frame. Using the relationship between runoff and DOC concentration, we estimated historical DOC export between 1995-2015. Large inter-annual variability in runoff generation (Figure 3-3) led to large inter annual variability in DOC export (estimated range between 0.5 and 2.5 g C m^{-2} per year). At the end of the freshet, cumulative SC DOC export in 2016 (65 %) was more than 1.5 greater than historical average (41 %, Figure 3-7b). In other years, cumulative DOC export by the end of the summer was more than 3 times greater than export in 2016.

3.4 Discussion

Both catchments behaved similarly throughout the season in terms of DOC concentration and composition and runoff generation. No clear impact of wildfire was evident in the comparison, with the possible exception of increased DOC export during summer in the burned catchment. However, our study strongly highlights the importance of the spring freshet for understanding the controls on catchment export of DOC both in terms of quantity and composition.

3.4.1 Seasonal shifts in runoff sources and DOC composition

Runoff was a strong control on DOC concentration and composition, and this relationship was dependent on season (Figure 3-5). Seasonal shifts in DOC quality have been well documented in similar studies (Broder et al., 2017; Fellman et al., 2009;

Larouche et al., 2015; Vonk et al., 2015 and references within), but due to infrequent data collection during snowmelt, most studies separate DOC quality into snowmelt and summer seasons only. End member mixing analysis allowed us to estimate three seasonal shifts in DOC sources to the catchment outlet: early spring, late spring, and summer (Figure 3-6). At both SC and NW, snowmelt was responsible for > 70 % runoff generation, with the remaining contribution coming from organic soil porewater during early spring. The DOC originating from organic soil porewater in this early spring period was of high aromaticity (Figure 3-4e and Figure 3-4f), likely due to runoff generation coming primarily from near-surface organic soils in peatlands. As the freshet progressed, there was a rapid increase in $S_{275-295}$, which corresponds to increased contributions of LMW DOC (Figure 3-4e). The larger DOC compounds are likely exported during high velocity flow, while smaller compounds dominate export as snowmelt is slowly exhausted. Also during late spring, organic soil porewater, diluted by precipitation, dominated DOC sources reaching the catchment outlet (Figure 3-6), and DOC was exported in greater concentration than during early spring (Figure 3-5b). Dissolved organic carbon exported from organic soil porewater during late spring has been shown to be more microbially labile than organic soil porewater DOC in the summer or fall (Chapter 2), due to lower biotic demand during cooler springtime temperatures, winter preservation of labile DOC compounds, and shallow flow paths impeding groundwater influence (Fellman et al., 2009; Connon et al., 2015). Warming temperatures and changing precipitation patterns in northern climates have caused increased winter precipitation, warmer soil temperatures, and a greater net ground heat flux (IPCC, 2007; Schuur et al., 2008; Quinton et al., 2009). Together, these perturbations may prevent complete fall freeze-up of the active layer (Schuur et al., 2008), and thus microbial activity over the winter months could reduce the pool of labile compounds available for export during the spring freshet. On the other hand, microbial activity occurring later in the season could increase the pool of labile DOC preserved over the winter.

Groundwater DOC typically exists in concentrations around 5 mg C L^{-1} (Olefeldt and Roulet, 2014), while peatland porewater DOC can exceed 100 mg C L^{-1} (Chapter 2). Organic soil porewater exported after the freshet is highly aromatic and microbially recalcitrant (Chapter 2). After the freshet, groundwater dominated runoff production, yet we still see DOC around 25-30 mg C L^{-1} (Figure 3-6) suggesting some inputs from upstream organic soil porewater. We also observed lower SUVA in summer compared to early and late spring (Figure 3-4e), which is consistent with a co-domination of DOC by groundwater and organic soil porewater (Figure 6). Groundwater SUVA typically does not exceed 2 L mg C^{-1} m^{-1} (Shen et al., 2015; Olefeldt and Roulet, 2014), while organic soil porewater SUVA can be >4 L mg C^{-1} m^{-1} (Chapter 2). Despite low SUVA, summer DOC in both catchments was likely not biolabile. We have shown that organic soil porewater is not microbially available during the summer (Chapter 2) likely due to higher turnover rates of freshly produced DOC associated with enhanced microbial activity and hydrologic isolation during low flow. Additionally, aromatic DOC compounds adsorb to mineral soils where they are used and processed by microbes and incorporated into microbial biomass (Kaiser and Kalbitz, 2012). Once this DOC leaches into the hydrosphere, it is of low aromaticity, yet microbially recalcitrant (Kaiser and Kalbitz, 2012). Therefore, while low aromaticity and low SUVA are typical of biolabile DOC compounds in near-surface organic soils (Wright and Reddy, 2009), this does not hold true for DOC exiting groundwater sources. Because aromatic structures are the primary UV-light absorbing compounds in water (Corin et al., 1996), this groundwater-supplied summer DOC is also likely not susceptible to photochemical degradation.

3.4.2 Impacts of wildfire on DOC composition at the catchment outlet

Wildfires affect biogeochemical cycles through alterations to albedo, soil temperature and moisture, vegetation, and nutrient availability (Zoltai et al., 1998; Flannigan et al., 2008; Olefeldt et al., 2013a; Olefeldt et al., 2013b; Chapter 2). On recently burned peat plateaus and sites located at the boundary between permafrost peat plateaus and mature thermokarst bogs in the discontinuous permafrost zone, porewater DOC SUVA was 30 – 50 % higher and biodegradability was reduced by up to 50 % when compared to intact peat plateaus or thermokarst wetlands, respectively (Chapter 2). However, at the catchment outlet, SUVA values were higher at SC than at NW during the spring, suggesting minimal influence of wildfire on organic soil porewater DOC composition during this time frame (Figure 3-4 and Figure 3-5). In the summer, SUVA values were slightly greater at NW than SC, which is consistent with increased SUVA after a wildfire observed in organic soil porewater (Chapter 2). However, we know that during the summer downstream connectivity to burned upland and peatland sources is likely limited, and this increased SUVA may be independent of the influence of wildfire. It is possible that DOC processes that occur in transport, such as microbial and photochemical transformations, atmospheric evasion, and flocculation (Cory and Kaplan, 2012; von Wachenfeldt et al., 2009), in conjunction with summer runoff supply mixing with low SUVA groundwater sources, have a greater control on DOC characteristics at the catchment outlet than does disturbance. Our results thus suggest that wildfire is unlikely to have a major effect on catchment DOC export or DOC composition.

3.4.3 Runoff and DOC export

Although runoff exhibits large interannual variability (Figure 3), there has been a significant increase in streamflow at SC since 1995 primarily due to permafrost thaw (St. Jacques and Sauchyn, 2009). This recent permafrost thaw has likely increased the connectivity of organic soil porewater to catchment outlets, and due to the high aromaticity and high concentration of organic soil porewater DOC, thaw may increase aromatic DOC export proportionally more than observed increases in runoff. The spring freshet dominated the 2016 study season at both catchments, and summer baseflow was low compared to historical averages (Figure 3-3). However, in years where there are summer storms, we are likely to observe more DOC originating from organic soil porewater reaching the catchment outlet, which, in high concentration, could fuel downstream productivity. Because it is linked to discharge (Eq. 1), the majority of annual DOC export in 2016 had occurred by the end of the freshet. In fact, the 2016 freshet exported > 50 % more DOC than our estimates of the historical average (Figure 7a and b). However, our estimates assume that the DOC-runoff relationship has remained constant over this time period, despite potential increases in hydrological connectivity from thermokarst bogs. Thus, the estimates of historical DOC export, particularly in the summer, may be inaccurate. Climate warming is expected to impact runoff and DOC characteristics in northern climates well into the next century (IPCC, 2007; Schuur et al., 2008). Because greater snowfall is predicted in high latitude ecosystems with climate warming (IPCC, 2007), there is likely more snow available for melt during the spring freshet. Together, permafrost thaw and enhanced winter snowfall likely work together to enhance runoff generation in northern climates.

While there was no discernable influence of wildfire on DOC composition (Figure 3-4 and Figure 3-5), DOC export from July to September was greater at NW than at SC (Figure 3-7a). Because wildfire removes surface vegetation, burns off the upper layer of peat and reduces albedo, it enhances ground heat flux (Zoltai et al., 1998; Schurr et al., 2008). It has recently been determined that wildfire directly causes active layer deepening (Gibson, 2017) and creates a new supply of water available for export, which can thereby enhance DOC export off of burned catchments - an observation that is consistent with our results. However, further studies on this matter are required.

3.5 Conclusion

We show that DOC composition is linked to its origin, and that shifts in DOC source occur over short-time frames, reiterating the need for high-resolution data collection. The early spring period is traditionally understudied in permafrost regions, yet, despite only lasting a few days, is responsible for more than a quarter of annual DOC export into downstream aquatic ecosystems, and we have shown this DOC to be of unique water quality. Additionally, the late spring period is responsible for a disproportionately large fraction of annual DOC export. The DOC exported during late spring is of high molecular weight and derived almost entirely from near surface organic soils, which, in a previous study, have been shown to be of high biolability. We show that there is little to no effect of wildfire on DOC composition at the catchment outlet, despite the fact that most of the upland forests and peat plateaus were burned in the wildfire, suggesting that a majority of DOC is not derived from absolutely fresh plant material, even in the unburned catchment. Higher DOC export during summer low-flow periods reaching the outlet of a burned catchment may be linked to wildfire-accelerated active layer thaw creating an additional DOC source, but further studies on this matter are required.

As temperatures increase and precipitation patterns shift in high-latitude ecosystems, we can expect to see shifts in runoff production and thus DOC export. These shifts are likely to impact DOC export characteristics, in terms of magnitude, composition, and quantity of export. We have shown that DOC export from peatland-rich catchments in the discontinuous permafrost zone of western Canada is more likely to be influenced by climate-mediated effects on runoff generation and permafrost thaw rather than by be affected by wildfire.

3.6 References

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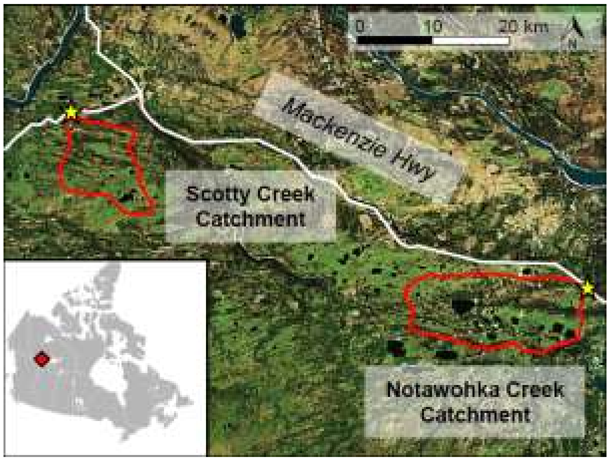

Figure 3-1. Scotty Creek and Notawohka Creek catchments in western Canada with sampling locations indicated by yellow stars where the creeks cross the highway. Photo source: Zoom Earth MODIS Satellite.

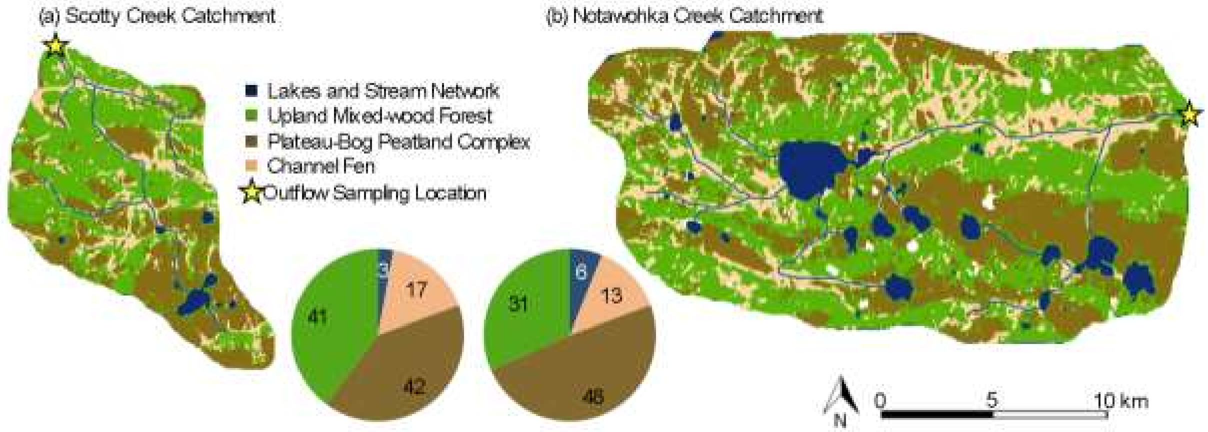

Figure 3-2. Supervised classification through ArcGIS used maximum likelihood classification to characterize land cover of a) SC and b) NW catchments, where pie charts represent % land cover.

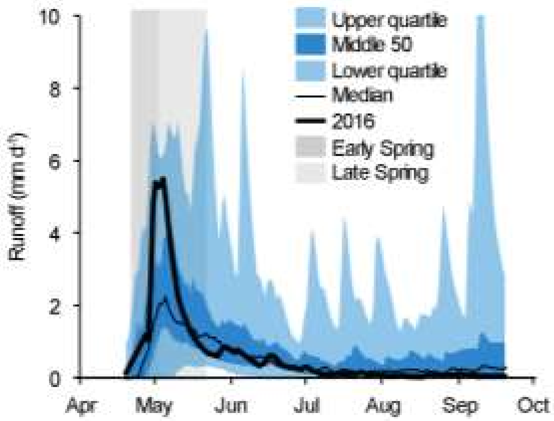

Figure 3-3. Historical runoff at SC between 1995-2015. Runoff generation during the 2016 study period was in the upper quartile during the freshet, but due to a lack of summer storms, summer runoff generation was in the lower quartile.

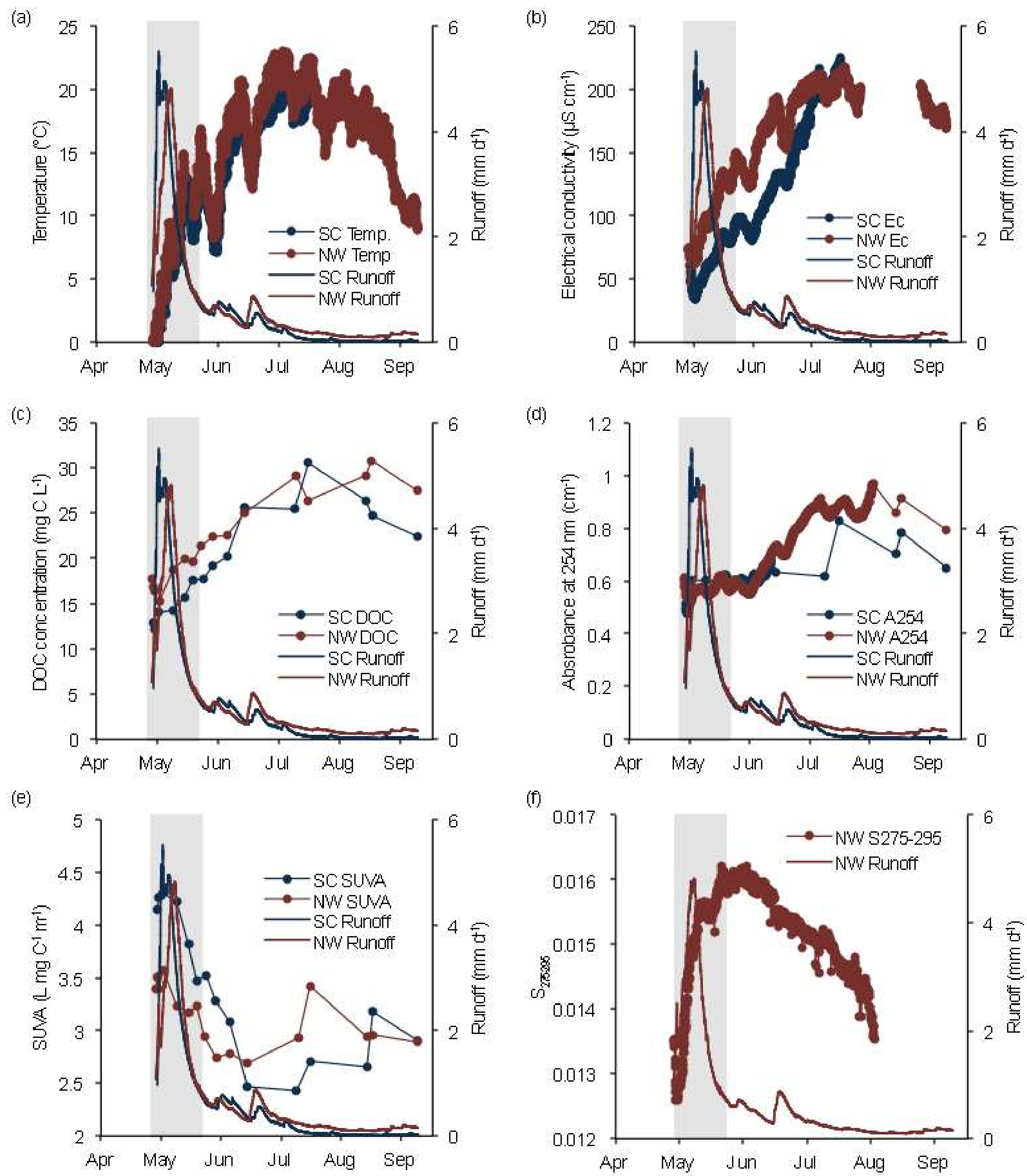

Figure 3-4. Seasonal runoff and a) temperature, b) electrical conductivity (µS cm $^{-1}$), c) DOC concentration (mg C L $^{-1}$), d) A_{254nm} (m $^{-1}$), SUVA (L mg C $^{-1}$ m $^{-1}$), and f) $S_{275\text{-}295}$. The shaded grey area indicates the freshet. The EC logger at NW was removed in late July, while a lack of flowing water at SC in August caused a loss of data.

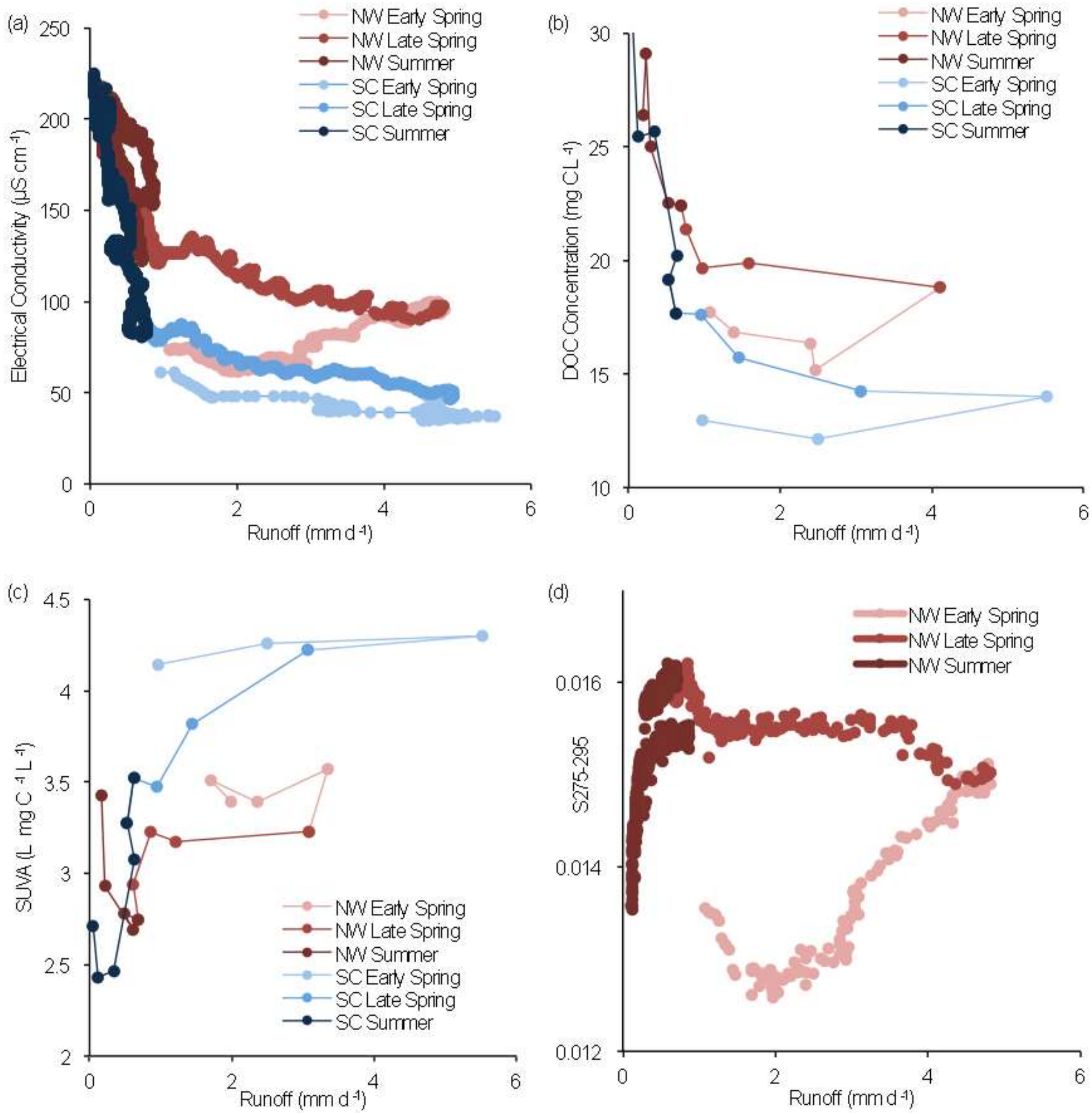

Figure 3-5. Water chemistry and quality parameters a) EC (µS cm $^{-1}$), b) DOC concentration (mg C L $^{-1}$), c) SUVA (L mg C $^{-1}$ m $^{-1}$) and d) $S_{275\text{-}295}$ as a function of runoff.

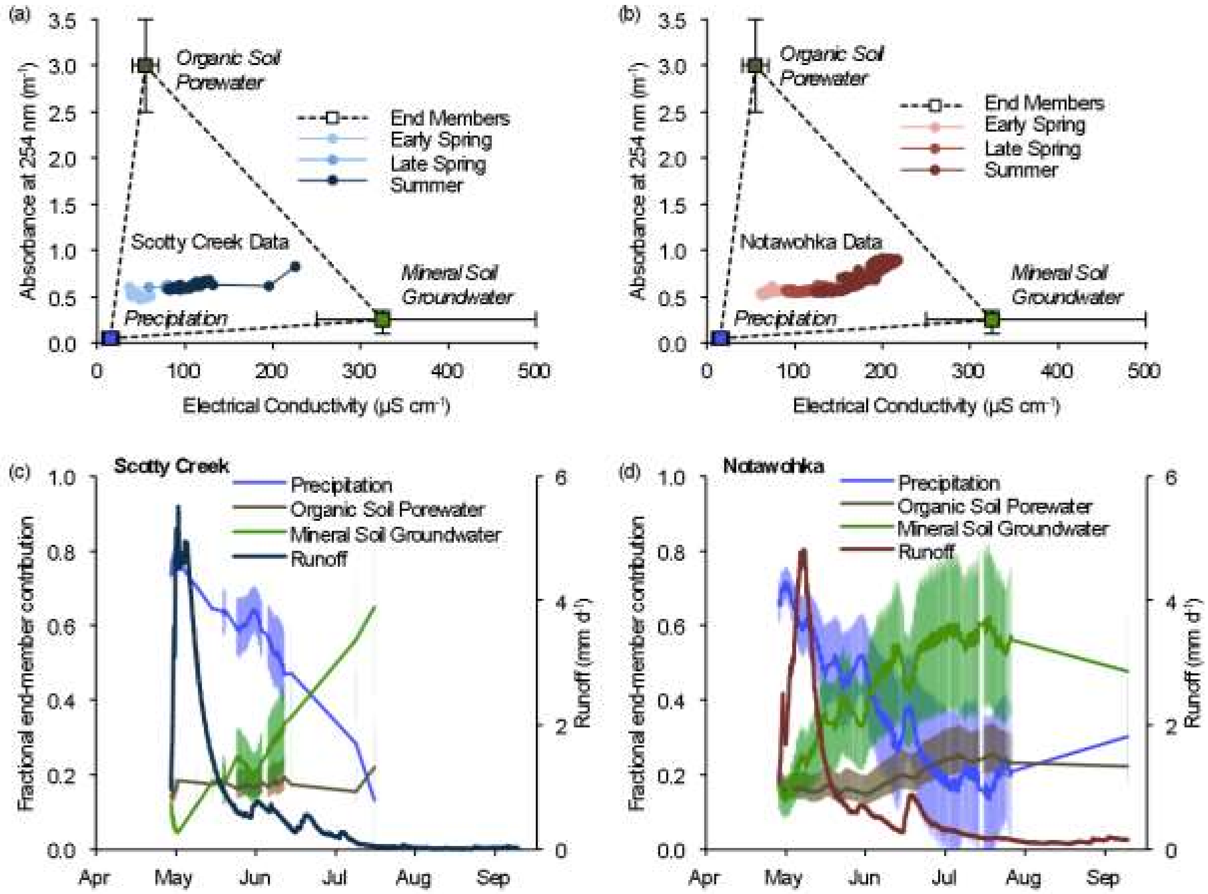

Figure 3-6. Fractional runoff contribution at SC and NW as indicated by stream-flow separation using end member mixing space defined by A_{254} and EC.

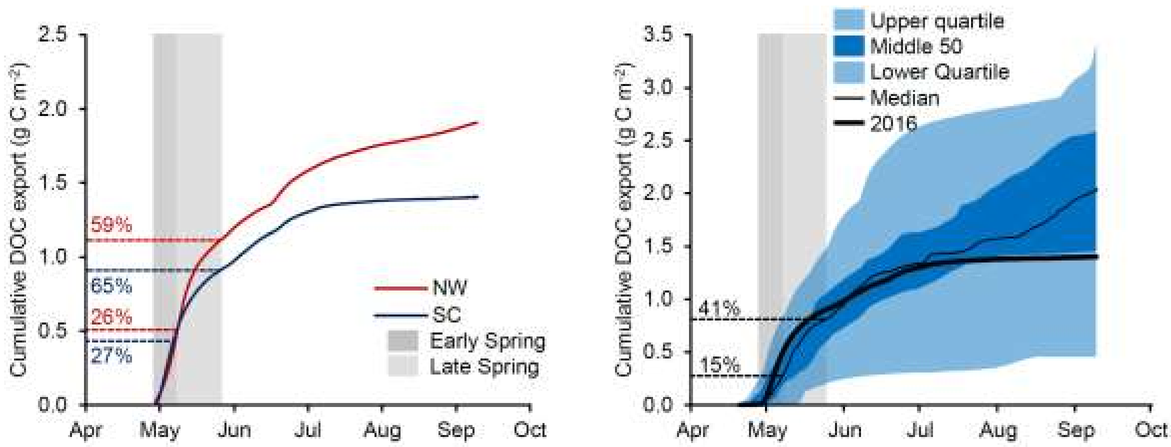

Figure 3-7. Cumulative DOC export a) during 2016 at NW and SC, and b) over a 20 year historical period ranging from 1995-2015.

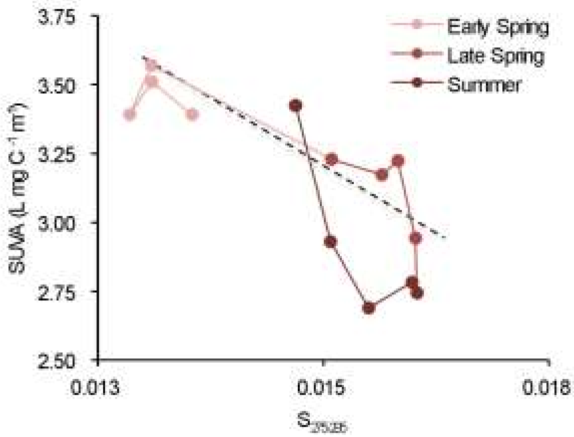

Figure S3-1. Specific UV-absorbance vs. $S_{275-295}$ at NW. Specific UV-absorbance was calculated from DOC and absorbance values collected via grab samples, while $S_{275-295}$ was calculated from continuous absorbance samples collected by the spectrophotometer (R^2=0.64, p=0.03).

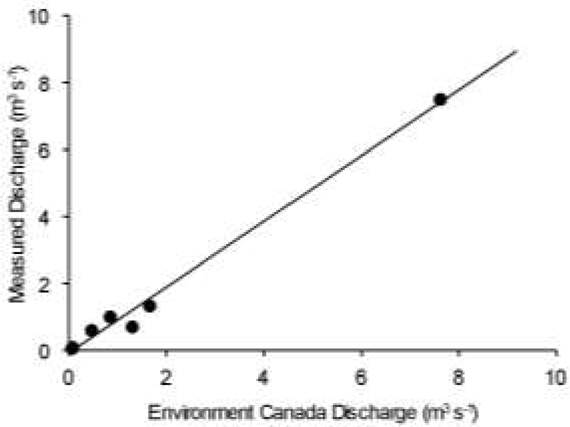

Figure S3-2. Instantaneous discharge measurements calculated using the velocity-area method at six sampling occasions had a strong linear correlation (R^2=0.99) to discharge measurements obtained by Environment Canada at Scotty Creek (wateroffice.ec.gc.ca).

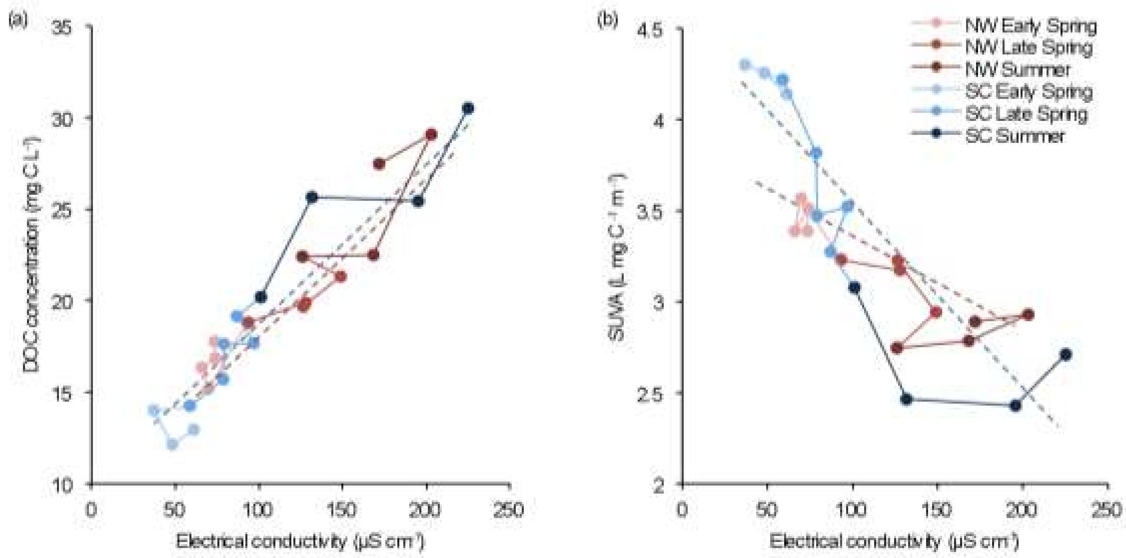

Figure S3-3. Seasonal trends in the correlation between EC (µS cm $^{-1}$) and a) DOC concentration (mg C L $^{-1}$) and b) SUVA (L mg C $^{-1}$ m^{-1}).

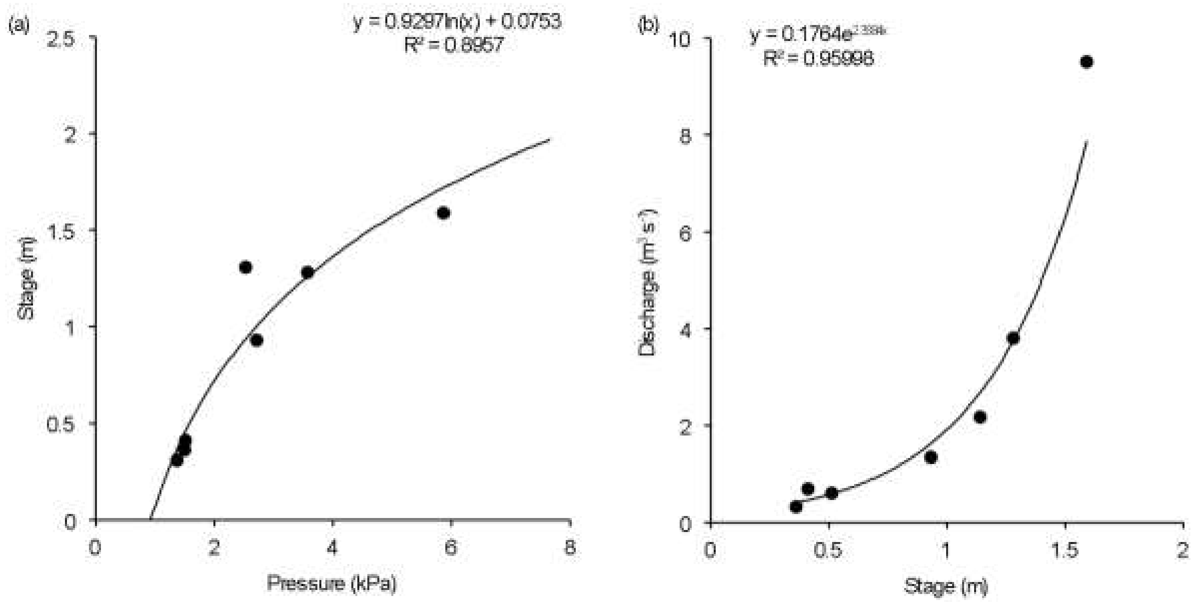

Figure S3-4. Notawohka Creek catchment a) stage vs. pressure and b) discharge vs. stage rating curves. Pressure is calculated as the different between water and air pressure. Stage at peak flow, determined by pressure, was 34cm higher than our maximum measured stage.

4.0 Conclusions

4.1 Research objectives

We conducted this research to better understand how vulnerable subarctic aquatic ecosystems are responding to a warming climate: more specifically how they might be affected by wildfire and permafrost thaw in upstream peatlands. The overarching objective of our research was to determine (1) how wildfire and permafrost thaw in peatlands impact DOC susceptibility to transformations, (2) if the impact of wildfire is observed at the catchment outlet, and (3) if wildfire or shifts in hydrology are likely to have a more pronounced effect on landscape carbon cycling.

4.2 Conclusions

In chapter 2, our results show that in the spring permafrost thaw enhances biodegradability, while the effect of wildfire was opposite. However, the catchment is most hydrologically well connected in this time period, and this is when the majority of annual DOC export occurs. Therefore, the impacts of disturbance on peatland porewater biodegradability likely influence regional and annual carbon cycling, despite only being observed in the spring. In the summer and fall, we show that DOC susceptibility to transformations is not linked to composition, and thus there is little impact of disturbance later in the season, when BDOC is also minimal and runoff generation is limited. Finally, our results show that photodegradation is an important transformative process in the summer, and with longer ice-free seasons expected due to climate warming, photodegradation is likely to become a more important component of freshwater carbon cycling in the future.

In chapter 3, our results highlight the necessity of high-resolution data collection to capture short-lived shifts in DOC composition and export. We show that the spring period is responsible for a disproportionately large portion of annual DOC export, and results from chapter 2 suggest it is highly labile during this time frame. The spring period plays a role in annual and regional carbon cycling, yet is traditionally understudied in high-latitude catchments. Finally, our results show that in contrast to the effects of wildfire on peatland porewater DOC, there is no clear influence of wildfire on DOC composition at the catchment outlet which was consistent with our data on porewater characteristics. However, wildfire may be responsible for increased DOC export during the summer, due to deeper seasonally thawed layers creating groundwater connections, but this requires further studies.

With warming temperatures in northern climates associated with climate change, we expect to see the formation of more thermokarst wetlands and more frequent and severe fires (Kasischke and Turetsky, 2006; Flannigan et al., 2008; Tarnocai, 2009), both of which affect DOC composition and character. Additionally, shifts in hydrologic connectivity and subsurface flow paths are expected to occur as a function of permafrost thaw (St. Jacques and Sauchyn, 2009). Because the discontinuous permafrost zone is the most vulnerable to climate change (McClymont et al., 2013), continuous data monitoring of these ecosystems is vital to better understand the impacts of climate change on DOC cycling and downstream ecosystem productivity. Finally, DOC acts as a vector for nutrients and contaminants (Wright and Reddy, 2009; McDowell et al., 2006), and therefore shifts in composition and quantity of exported DOC is likely to have profound impacts on downstream ecosystems.

4.3 Future work

Instruments with continuous data collection capabilities were deployed to capture shifts in DOC characteristics following short-lived storm events. However, there were no summer storms in 2016, and future studies will hopefully be conducted in years with typical precipitation patterns. Additionally, porewater collection was carried out during late spring (Figure 2-3), and we therefore can only speak about DOC lability in early spring based on measured and calculated indices. If another incubation study is to be conducted, porewater collection should occur at the onset of the spring freshet to better capture early spring DOC lability. Finally, future work should consider examining how disturbances may impact nutrient and contaminant export in the discontinuous permafrost zone of western Canada.

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