Source and fate of dissolved organic matter in boreal headwater streams

by

Karl Friesen-Hughes

A thesis submitted to the University of Winnipeg in partial fulfillment of the requirements for the Master of Science in Bioscience, Technology and Public Policy

Department of Biology

Master of Science in Bioscience, Technology and Public Policy

The University of Winnipeg

Winnipeg, Manitoba, Canada

May 2023

Abstract

Understanding the source and fate of dissolved organic matter (DOM), a key water quality variable, in boreal headwaters is of critical importance considering the amount of carbon stored and processed in different ecosystem components within the boreal forest and the sensitivity of these processes to climate change. Using historical streamflow and stream chemistry data in combination with direct measurements of the landscape sources of DOM and more detailed stream DOM quality data from 2021 at the IISD-ELA, I examined how the terrestrial source of DOM influences the quantity and quality of DOM in three boreal headwater streams. Using historical stream data from 1981-2021, I found that concentration-discharge (c-Q) relationships varied based on both catchment characteristics and hydrological conditions. Streams draining upland-dominated catchments were more often transport-limited (i.e., concentration increased with increasing flow), whereas a wetland-dominated stream was more often source-limited (i.e., concentration decreased with increasing flow) in terms of stream DOM concentration. DOM concentration and quality data in soil leachate indicated that streamwater had DOM characteristics suggesting it originated from near-stream organic soils, while after the drought the DOM came proportionally more from distal mineral soils (in addition to near-stream organic soil contributions). I showed that the severe drought in 2021 made streams with varying landscape characteristics respond similarly to the post-drought flush. These findings also illustrate that while c-Q relationships may be different among streams draining upland-dominated and wetland-dominated catchments as a result of the different abilities of these landscape to accumulate and mobilize DOM,

DOM quality responded to this drought to post-drought flush synchronously among all three streams. As climate change will alter the frequency, duration, and severity of future hydrological conditions, this has repercussions for the DOM dynamics in headwater streams and the resulting water quality downstream.

Co-Authorship Statement

This thesis is based on one manuscript which will be submitted for publication. Karl Friesen-Hughes, who led the definition of the research problem, formulation of study design and field equipment, sample collection and analysis, data analysis, and interpretation of results and writing of the manuscript, will be the lead author on this manuscript. Dr. Nora J. Casson, who contributed to the definition of the research problem, formulation of study design, analytical approach, results interpretation, and editorial guidance on the writing will be a co-author on this manuscript. Dr. Henry F. Wilson, who supported spectrofluorometric analysis on 2021 water samples, will be a co-author on this manuscript.

Acknowledgments

I would like to acknowledge that this research was conducted at IISD-ELA which is located in Treaty 3 territory, the traditional land of the Anishinaabe Nation and the homeland of the Métis Nation. Additionally, I would like to acknowledge that I have written this thesis primarily in Winnipeg, in Treaty 1 territory, in the heartland of the Métis Nation, and on the land of the Anishinaabeg, Cree, Dakota, Dene, and Oji-Cree people, who lived here before us and continue to live here. I want to also acknowledge that our water is sourced from Shaol Lake 40 First Nation.

I would like to thank Dr. Nora Casson – if that is even possible in words. She has supported me infinitely despite any speedbumps the world put in front of me, or any speedbumps that I ran into myself. She is endlessly positive, kind, patient, intelligent and she is a person that everyone should look up to. I first took a course with Dr. Casson in Fall 2018 and have been working with her ever since May 2019. It is an understatement to say I would not be here today if not for her. She is the best mentor I could ever ask her and I feel incredibly lucky to have had her support for all these years.

I would also like to thank my committee members Dr. Darshani Kumaragamage and Dr. Kara Webster for their ongoing support and feedback on this project. Thank you both for your invaluable contributions to this research.

I would like to thank everyone at IISD-ELA who supported this research. Dr. Scott Higgins, for showing me the ropes and supporting me in any way he could whenever I was out at camp. Also, for his support and feedback on this thesis through his role as my external examiner. Dr. Sonya Havens and Blake Cooney for supporting me with any and all laboratory related needs that I had throughout this process, as well as any

other staff who helped to collect and support my stream sample collection. Chris Hay and Ken Sandilands for supporting my use of the IISD-ELA long-term data and my countless data questions. Roger Mollot, Pauline Gerrard, and Lee Hrenchuk for always finding me a place to stay at camp and supporting me while I was there. And I would like to thank everyone else at IISD-ELA who contributed in smaller ways – each and everyone there is a part of what makes doing research there such a magical experience. I will cherish all of my memories and all of the connections I shared from that time.

Next I would like to thank every person who helped me in the field at IISD-ELA. Dr. Matt Q. Morison, Bailey Pavcek, Tyler Winsor, Richard La, and Dylan McKenzie, this work would not have been possible without you. Matt, thank you for being so resilient and helping me conduct field work during some pretty strange and difficult times. One of our trips there, I were two of four people on camp, which was a surreal experience. This also meant that on top of some pretty back-breaking field days, I still had to cook for ourselves once I got home. Another trip, I were fortunate enough to spend in the famed Schindler Cabin, literally standing on the shoulders of giants in a place built by a man who was a very prominent figure in both IISD-ELA and limnology as a whole. Bailey, thank you for being such a rock. I will never forget our time at IISD-ELA, and I couldn't have asked for better help out there. Thanks for helping me smarten up, buddy. Tyler, I had some good times boating across 239. I think the trip was a slam-dunk. Richard, I really appreciate your time as well. I'm so grateful that I got to bring you out there for the first time, and I can't wait to see what you learn from your research. Good luck! Dylan, thank you for all of your help too. You definitely went out of your way to be

as helpful as possible, and all this despite how busy you were. I can't thank you all enough!

I would also like to thank Dr. Henry Wilson and Marilyn Makortoff for allowing me to conduct spectrofluorometric analysis on my water samples and training me how to use the Horiba Aqualog. This was a critical step in learning more about the quality of DOM, which was a cornerstone of this project.

Thank you to Paul Mann for all of your help in the soils lab over the years. You helped so much with the construction of the lysimeters and with so many other miscellaneous things to do with my project. I really appreciate your guidance, expertise, and willingness to take time out of your day to help with my project. Also thank you to Alex Wiebe for help in the design stage of the lysimeters.

A warm thank you also the Water Quality Lab and every member who has been a part of it while I've been around. I'm so grateful to be a part of this group, and I thank each and every one of your for all of your support and guidance over the years.

Thank you to Chelsea Lobson and Lake Winnipeg Foundation for supporting me in this final chapter of my thesis. I'm so excited to be a part of the organization, and I'm eternally grateful for your support while I completed my thesis.

I would also like to acknowledge that this research was funded by multiple scholarships. I personally received funding through the The University of Winnipeg Graduate Studies Scholarship (2020-2021), a Canada Graduate Scholarship - Natural Sciences and Engineering Research Council of Canada (NSERC) (2021-2022). Additionally, the costs of this research were funded by an NSERC Discovery Grant provided through Dr. Casson. Without this support, I could not have accomplished any of this.

Finally, I would like to thank my partner, Daryn, who has been there for me through this entire process. She has been an absolute pillar and deserves so much credit for her endless support which enabled me to take this project from start to finish. Thank you also to Rupert, for being a good lizard. My parents and siblings were always very supportive of my academic journey and I would not be here without them. Thank you to all of my family and friends for all of your support over the years. This experience has been one of ups and downs, and I wouldn’t be here if not for the great people in my life.

One last shout-out to Adriene Mishler AKA Yoga with Adriene for helping me to bow to the light and keep my body moving through many of the lockdowns. I’ve done an obscene amount of yoga with her over the years, and I owe her so much!

If it takes a village to raise a child, it also takes a village to create a thesis. There were so many people that had a hand in this work, and I appreciate each and every contribution made. It sincerely would not have been possible without all of you. Thank you.

Table of Contents

Table of Figures

Table of Supplemental Figures and Tables

1. General Introduction

1.1 Dissolved organic matter

Dissolved organic matter (DOM) is most commonly defined as the fraction of organic matter in dissolved form which passes through a 0.45 μm filter (Thurman, 1985; Zsolnay, 2003; Akkanen et al., 2012). DOM is a complex mixture of soluble organic molecules and compounds (Jaffé et al., 2008), originating from vegetation, root exudates, plant litter, soil humus, and microbial biomass (McDowell & Fisher, 1976; Thurman, 1985; Guggenberger & Zech, 1994; Mueller et al., 2016; Chen et al., 2017). DOM contains primarily carbon (i.e., dissolved organic carbon [DOC], a term which is often used interchangeably with DOM in the literature, which refers specifically to the carbon fraction of DOM), but also smaller proportions of macronutrients nitrogen, phosphorus, and sulfur, as well as micronutrients such as iron and toxic contaminants such as mercury (Maranger & Pullin, 2003; Qualls & Richardson, 2003; Ravichandran, 2004; Ged & Boyer, 2013). DOM represents the largest component of carbon flux to lakes from watersheds and atmospheric sources (Emmerton et al., 2019). While DOM is only a fraction of total soil organic matter, its mobility and reactivity makes it biogeochemically relevant for downstream ecosystems (Kalbitz et al., 2000; Chantigny, 2003; McDowell, 2003; Zsolnay, 2003; Battin et al., 2008; Fellman et al., 2009; Tank et al., 2010; Aiken et al., 2011; Bolan et al., 2011; Kaplan & Cory, 2016; Rodríguez-Cardona et al., 2021). In particular, DOM quantity and quality influences light regime and aquatic ecosystems (Pattanaik et al., 2010; Kritzberg et al., 2019; Webb et al., 2019), food web dynamics (Mierle et al., 1991; Williamson et al., 1999; Karlsson et al., 2012), organic pollutant and trace metal dynamics (Haitzer et al., 1998; Lawlor & Tipping, 2003; Dawson et al., 2009; Tugulea et al., 2018), water acidification (Erlandsson et al., 2011; Valinia et al., 2014), water quality and water treatment processing and costs (Ledesma et al., 2012; Lavonen et al., 2013; Ritson et al., 2014)

1.2 Headwater streams and DOM

Inland surface waters like lakes, rivers, and streams, are important contributors to the global carbon cycle, as they collect, process, and transport DOM from the landscape. Headwater streams are a critical means by which DOM enters the inland aquatic system. Despite their individually small scale, headwater streams make up an intricate network of DOM receptors across the terrestrial landscape. Due to their intrinsic density and length in comparison to larger aquatic systems, headwater streams often make up the majority of total river length (Bishop et al., 2008). These streams also have relatively high surface area to water volume ratios, meaning they receive disproportionately high quantities of terrestrial DOM (Ågren et al., 2007; Raymond et al., 2016) which is a highly chromophoric mixture of different molecules and compounds derived from various landscape sources (Sleighter et al., 2014; Mosher et al., 2015). Additionally, headwater provide a unique opportunity to study the influence of specific landscape units as they tend to be more homogeneous compared to larger catchments (Köhler et al., 2008).

1.3 The boreal forest is a globally relevant source of carbon containing many headwater streams

Northern ecosystems store large amounts of organic matter in soils, peat, plant biomass, and freshwaters (Gorham, 1991; Tarnocai et al., 2009; Pan et al., 2011; Hugelius et al., 2014). The boreal forest contains 272 ± 23 Pg of carbon, with 60% of the carbon found in the soils (Pan et al., 2011). A large component of that carbon is stored in organic soils and peatlands (Turanen et al., 2002; Limpens et al., 2008; Yu et al., 2010). Variability in carbon flux from soils to surface waters often determines whether an aquatic or terrestrial ecosystem functions as a source or sink of carbon (Waddington & Roulet, 2000; Roulet et al., 2007). Carbon also varies vertically throughout boreal soils, with increasing age, decomposition, and recalcitrance with depth (Ruess et al., 2003; O'Donnell et al., 2011) due to the gradual accumulation of carbon through moss, root production, and vegetation burial over time (Trumbore & Harden, 1997). Compared to other biomes, boreal forests also have higher proportions of headwater streams (Horton, 1945; Bishop et al., 2008; Raymond et al., 2013). The sheer size of both carbon sources and headwater stream extents makes boreal forests of particular interest in the context of both the global carbon cycle and stream DOM dynamics. Boreal surface waters play a significant role in processing DOM from the landscape on a regional and global C scale (Cole et al., 2007; Tranvik et al., 2009).

1.4 Climate change is altering DOM cycling in the boreal headwater streams

The boreal forest is experiencing the most significant temperature increase of all forest biomes in the 21st century (IPCC, 2013; Price et al., 2013; Gauthier et al., 2015). Mean annual temperatures have increased by ~1.5°C since 1900 across most of the boreal forest (Price et al., 2013), and this region could increase by another 4-11°C by the year 2100 (World Bank, 2014). While increases in DOC concentration have often been linked to increases in temperature (Freeman et al., 2001; Evans et al., 2006; Kane et al., 2006; Laudon et al., 2012; Kane et al., 2014), the hydrological changes inherent to climate change are of particular relevance for the DOM dynamics in headwater streams. The quantity and quality of DOM in headwater streams is a direct result of the interaction between hydrology and landscape sources contained in headwater catchments. Hydrology is particularly vulnerable to climate change (Battin et al., 2009), as changes to precipitation, streamflow, water flowpaths, and hydrological connectivity are all expected outcomes (Stocker et al., 2013). There is also predicted to be an increased frequency and intensity of extreme weather events such as storms and droughts (Hansen et al., 2012; IPCC, 2013), as well as hydrological intensification (Creed et al., 2015a). Hydrological changes such as these inherently influence the way that DOM goes from land to waters, and the resulting quantity and quality of DOM in headwater streams (Pagano et al., 2014). Increased precipitation enhances DOM export from terrestrial landscapes to surface waters (Evans et al., 2005; Tranvik et al., 2009), and predicted shifts in seasonal timing of events may shift both the quantity and quality of DOM received downstream. Hydrological intensification can influence the transport and transformation of DOM (Raymond & Saiers, 2010). In northern regions, one consequence of climate change is that the proportion of both water and DOM export are increasing in winter and decreasing during spring and summer (Laudon et al., 2013). Seasonal changes to DOM export are important because in combination with the environmental conditions, this dictates the potential sources and fates of DOM. In addition to mobilization process changes induced by climate change, the changing environmental factors may also influence the quality and composition of DOM as it is transported from the landscape to surface waters (Battin et al., 2008; Manzoni & Porporato, 2011).

2. Introduction

2.1DOM in headwater streams

Carbon flows within and across inland environments through surface water, soil water, groundwater, and streamwater via dissolved organic matter (DOM), which is a key component n the global carbon cycle (Battin et al., 2009; Tranvik et al., 2009). Headwater streams connect terrestrial landscapes and downstream water bodies (Rasilo et al., 2016; Fovet et al., 2020) as they receive, process, and transport DOM from their surrounding catchments. Headwater streams represent the dominant pathway for carbon via DOM to enter downstream water bodies in boreal ecosystem (Emmerton et al., 2019). DOM is a key water quality variable in surface waters (Kaplan & Cory, 2016), influencing food webs (Fisher & Likens, 1972; Vannote et al., 1980; Jansson et al., 2007), light regimes (Pattanaik et al., 2010), algal growth (Creed et al., 2018) and trace metal and organic pollutant dynamics (Haitzer et al., 1998; Lawlor & Tipping, 2003; Tugulea et al., 2018). Headwater streams compose large proportions of terrestrial stream networks (Alexander et al., 2007; Bishop et al., 2008; Downing, 2012), and their extensiveness makes them intrinsically difficult to understand at a finer resolution in the context of water quality and conservation management (Lowe & Likens, 2005; Nadeau & Rains, 2007). As well, headwater catchments provide a unique opportunity to study the influence of particular landscape units as they tend to be less heterogeneous than larger catchments (Köhler et al., 2008). The quantity and quality of DOM in headwater streams can inform us about both where the DOM came from on the landscape (Hood et al., 2006; Ågren et al., 2007; Broder et al., 2015; Birkel et al., 2017) as well as what impact it could have on downstream water quality (Parr et al., 2015; Raeke et al., 2017; Baker et al., 2021). By nature, DOM quantity and quality in headwater streams is particularly sensitive to change because of the intrinsic link between headwater streams and their surrounding landscape (Aitkenhead et al., 1999; Gomi et al., 2002; Mattsson et al., 2005; Jaffé et al., 2008; Yates et al., 2019; Wymore et al., 2021), a relationship which is stronger in smaller basins compared to larger river basins (Meyer & Wallace, 2001; Alexander et al., 2007; Meter et al., 2007). But since headwater catchments contain various spatial characteristics and configurations of landscape units (e.g., wetlands, forests), this results in different DOM quantity and quality among proximal streams.

2.2 Landscape sources of DOM

2.2.1 Spatial characteristics and soil indices

The spatial characteristics of catchments can tell us a lot about the potential landscape sources of DOM to downstream surface waters (Williamson et al., 2008; Brailsford et al., 2021), and the flowpaths that can transport this DOM to streams under different hydrological conditions (Lintern et al., 2018). Both quantity and quality of DOM depend on both proximity to source material and the potential environmental processing occurring (Hood et al., 2005; Coble, 2007; Helms et al., 2008). Although mean catchment slope doesn’t tell us directly about landscape sources of DOM, flatter landscapes tend to have higher water tables and greater potential to accumulate organic matter and form wetlands (Creed et al., 2003; Andersson & Nyberg, 2008). Stream DOC concentrations tend to be higher in streams draining flatter catchments with low mean slope (Eckhardt & Moore, 1990; Andersson & Nyberg, 2008; Li et al., 2015; Connolly et al., 2018; Musolff et al., 2018; Zarnetske et al., 2018; Jankowski & Schindler, 2019).

Topographic wetness index (TWI) is a spatial metric which is derived from the slope and flow accumulation at each cell of a digital elevation model and is a metric can indicate areas likely to be wetter (higher accumulation) in a catchment (Beven & Kirkby, 1979). Areas with high TWI tend to have greater potentials to accumulate DOM (Grabs et al., 2012; Ledesma et al., 2015) due to the intrinsic convergence of flow which may lead to waterlogging (Luke et al., 2007) and anaerobic conditions (LaCroix et al., 2019). In addition to higher potentials of accumulating DOM, areas with high TWI also tend to experience greater runoff and thus transport of DOM to streams in comparison to low-TWI zones (Werner et al., 2021). Stream DOC concentrations are highest in streams draining catchments with high mean TWI (Andersson & Nyberg, 2009; Musolff et al., 2018).

2.2.2 Wetlands

Wetlands typically possess high water tables and long water residence times, creating anaerobic conditions that favour slower decomposition rates and greater accumulation of organic matter (Eckhardt & Moore, 1990; Thomas, 1997; Waddington & Roulet, 1997; Gorham et al., 1998; Elder et al., 2000; Kayranli et al., 2010; Walker et al., 2012; Catalán et al., 2016; Hoyt et al., 2019; LaCroix et al., 2019). It is well established in the literature that the proportion of catchments comprised of wetlands drives stream DOC concentrations, with higher proportions of wetland being associated with higher stream DOC concentrations (Dillon & Molot, 1997; Hinton et al., 1998; Aitkenhead et al., 1999; Creed et al., 2003; Mulholland, 2003; Laudon et al., 2004; Ågren et al., 2007; Creed et al., 2008; Laudon et al., 2012; Walker et al., 2012; Winterdahl et al., 2014; Dick et al., 2015; Hytteborn et al., 2015; Monteith et al., 2015; Tiwari et al., 2017; Zarnetske et al., 2018; Casson et al., 2019). DOM quality in streams draining wetland-dominated boreal catchments is typically older and more recalcitrant compared with streams draining upland-dominated catchments (Laudon et al., 2011). However, the influence of wetlands on the DOM in headwater streams depends not only on areal coverage but also on the spatial arrangement of wetlands within a catchment (Laudon et al., 2011; Casson et al., 2019).

2.2.3 Riparian zones

In catchments without widespread wetland coverage, riparian zones are key contributors to the quantity of headwater stream DOM (Fiebig et al., 1990; Bishop et al., 1994; Grabs et al., 2012; Knorr, 2013; Ledesma et al., 2015; Musolff et al., 2018). Riparian zones often share similarities with wetlands in terms of their saturated soil biogeochemistry (Vidon, 2017), and their ability to accumulate soil organic matter due to their often-high water table (Grabs et al., 2012; Strohmeier et al., 2013; Ledesma et al., 2015; Ledesma et al., 2018a; Musolff et al., 2018; Ploum et al., 2020). Riparian organic-rich near-surface soil horizons are often the most important contributor to the DOM to headwater streams (Boyer et al., 1997; Findlay et al., 2001; Bishop et al., 2004; Inamdar et al., 2004; Winterdahl et al., 2011), as these soils accumulate organic matter in close proximity to streams, thus making the DOM more readily available and mobilizable to the stream network compared with more upland parts of the catchment (Bishop et al., 2004; Seibert et al., 2009; Ledesma et al., 2015; Musolff et al., 2018). This process is also magnified in headwater riparian zones, where soil-to-water ratios are highest in comparison to larger stream and river systems (Aitkenhead et al., 1999; Gomi et al., 2002; Mosher et al., 2015). Riparian zones can also contain wetlands, but these are often hidden under the forest canopy (Creed et al., 2003). Research from the Krycklan Catchment Study in Sweden indicates that DOM in boreal streams comes almost entirely from riparian wetlands (Laudon et al., 2011; Ledesma et al., 2018a). Previous research shows that DOM derived from riparian soils and wetlands is more aromatic compared to DOM from mineral, upland sources (Ågren et al., 2008a; Kothawala et al., 2015; Ledesma et al., 2018a; Pisani et al., 2020).

2.3 Streamflow and DOM dynamics

Although the size and extent of landscape sources of DOM are critical to streamwater DOM dynamics, their ability to behave as sources to streamwater depends on the hydrology of the landscape and the hydrological connectivity between sources and streams (Pacific et al., 2010; Inamdar et al., 2011; Voss et al., 2015). Concentration-discharge (c-Q) relationships in headwater streams are influenced by both sources and connectivity of those sources to streams, either decreasing with increasing flow (i.e., where DOM becomes diluted) or increasing with increasing flow [i.e., where DOM becomes enriched; Creed et al., 2015; Moatar et al., 2017)].

2.3.1 Wetlands

Streams draining wetland-dominated catchments typically experience dilution of DOM at high flow (Laudon et al., 2004; Laudon et al., 2011; Birkel et al., 2017). This is because hydrological additions mix with organic-rich wetland porewater, resulting in dilution of DOM in streamwater (Laudon et al., 2007; Vidon et al., 2010; Tiwari et al., 2019). Since wetlands have intrinsically high water tables, organic-rich near-surface soil horizons are generally always connected, regardless of additions of water (Schiff et al., 1998). Regardless of hydrological conditions and event characteristics, streams draining wetland-dominated catchments tend to have DOM dominated by near-stream sources (Ducharme et al., 2021).

2.3.2 Riparian zones

Unlike wetlands, riparian zones have more dynamic water tables, making the transport of DOM to streams more dependent on hydrological conditions. A critical feature of many northern riparian zones is the vertical decrease in saturated hydraulic conductivity with soil depth (Nyberg et al., 2001). This means that small additions of water can raise the water table to where lateral hydraulic conductivity is much higher, magnifying eventual export events (i.e., the transmissivity feedback mechanism) (Bishop et al., 2004; Bishop et al., 2011; Ledesma et al., 2018b). In combination with the organic-rich near-surface soil horizons, changes in flow can drive large changes in headwaters streams. Under lower flow conditions, the water table is lower, deeper riparian soils have lower hydraulic conductivity, and DOM export to streams is reduced; higher flow enables shallower riparian soils which have higher hydraulic conductivity (Bishop et al., 2004) to export greater amounts of DOM to streams (Hinton et al., 1998; Seibert et al., 2009; Laudon et al., 2011; Winterdahl et al., 2011). However, riparian zones have been found to be source areas to streams even during dry periods (Johnson et al., 1997; Stieglitz et al., 2003). High flow in catchments dominated by riparian wetlands can cause connection and activation of these sources of DOM to streams (Bishop et al., 2004; Seibert et al., 2009; Laudon et al., 2011; Dick et al., 2015; Ledesma et al., 2015).

2.3.3 Hydrological connectivity

In addition to landscape characteristics, DOM dynamics in headwater streams are also controlled by changes to the hydrological connectivity between the stream and the terrestrial sources of organic matter (Schiff et al., 1998; Singh et al., 2015; Birkel et al., 2017; Broder et al., 2017; Covino, 2017; Zimmer & McGlynn, 2018; Hale & Godsey, 2019; Wen et al., 2020; Blaurock et al., 2021; da Silva et al., 2021a; Werner et al., 2021). The hydrological connectivity between streams and catchment sources is heavily influenced by hydrological events such as storms and droughts (McDowell & Likens, 1988; Hornberger et al., 1994; Boyer et al., 1997; Raymond & Saiers, 2010), as well as the antecedent moisture conditions (McGuire & McDonnell, 2010; Penna et al., 2015; Blaurock et al., 2021). Increased hydrological connectivity between streams and wetlands tends to dilute DOM in streamwater since water is flushed from the landscape more quickly, mitigating both the contact time with wetland soils as well as the extent of processing which can occur (Schiff et al., 1998; Covino, 2017; Jeanneau et al., 2020). Lateral hydrological connectivity matters in terms of which sources across the landscape are connected to streams, but vertical connectivity matters for determining whether DOM is coming from deeper groundwater flowpaths or shallow subsurface flowpaths. DOM derived from deeper groundwater is typically less concentrated, less aromatic, and less humic than DOM derived from shallow subsurface soil horizons (Kalbitz et al., 2000; Fellman et al., 2009; Inamdar et al., 2011; Inamdar et al., 2012; Singh et al., 2014).

2.4 Knowledge gap and study impetus

2.4.1 The importance of studying DOM dynamics in the boreal forest

Understanding the source and fate of DOM is especially important in the boreal forest, the biome which stores more than a third of the world's terrestrial carbon (Bradshaw & Warkentin, 2015) in peatlands (Gorham, 1991) and below-ground stores (Pan et al., 2011). Elucidating the spatial distribution and pathways of landscape sources of streamwater DOM can help us understand biogeochemical activities in a given catchment (Pacific et al., 2010; Laudon et al., 2011), as well as the downstream output of DOM from headwater streams (Raymond & Saiers, 2010; Ågren et al., 2014; Peralta-Tapia et al., 2015), which has implications for atmospheric carbon fluxes (Hall et al., 2019) and water quality and water treatment (Ledesma et al., 2012; Lavonen et al., 2013; Ritson et al., 2014). There is a research need to further assess the spatiotemporal variability and drivers of the source and fate of DOM from landscapes to surface waters (Singh et al., 2015, Tunaley et al., 2016; Broder et al., 2017; Creed et al., 2018; Tank et al., 2018; Emmerton et al., 2019; Werner et al., 2019; Fork et al., 2020; Wardinski et al., 2022). Boreal watersheds contain various proportions and spatial arrangements of organic-rich wetland and riparian peat and soils and mineral upland soils. Although the existing literature shows relationships between landscape components (e.g., wetlands, riparian soils) and streamwater DOM in terms of DOC concentration, landscape sources of streamwater DOM are often inferred from streamwater DOM coupled with knowledge of catchment characteristics rather than measured directly. As well, the relationship between landscape sources of DOM and stream DOM quality is much less clear (Guarch-Ribot & Butturini, 2016; Broder et al., 2017; Yates et al., 2019; Sebestyen et al., 2021). Additionally, streamwater DOM dynamics can even differ among adjacent streams (Schiff et al., 1998; Temnerud & Bishop, 2005) sometimes even more than what is observed on a regional scale (Bishop et al., 2008); this is especially the case in higher order streams (Creed et al., 2015a). This is because the spatial properties and arrangement of headwater catchments controls how stream DOM dynamics respond to controlling factors (Clark et al., 2010; Laudon et al., 2011; Monteith et al., 2015). Research on the source and fate of DOM is rare in landscapes with both uplands and peatlands (Clark et al., 2008; Sebestyen et al., 2021), despite the variability in DOM composition (Ågren et al., 2008a; Köhler et al., 2009). Additionally, climate variables such as temperature and precipitation alter both the spatial arrangement of landscape sources of DOM and the hydrological mechanisms by which DOM is processed and transported to streams (Covino, 2017; Wen et al., 2020).

2.4.2 Climate change and boreal forest headwater stream DOM dynamics

Northern regions such as the boreal forest are projected to face more severe climate change, such as temperature increases and hydrological intensification (IPCC, 2014; Hansen et al., 2006; Kirtman et al., 2013; Abbott et al., 2016; Spinoni et al., 2018), making understanding the relationship between catchments and headwater streams increasingly important. It is uncertain how the terrestrial source of DOM influences both the quantity and quality of DOM downstream across heterogeneous boreal landscapes (Oswald et al., 2011; Laudon & Sponsellor, 2018; Creed et al., 2018; Yates et al., 2019; Fovet al., 2020; Wen et al., 2020; Gómez-Gener et al., 2021) and influences variability in concentration-discharge relationships (Oswald & Branfireun, 2014; Fork et al., 2020; Gómez-Gener et al., 2021). Another critical piece to this puzzle is understanding how climate drivers will influence the quantity and quality of DOM on its journey from land to surface waters (Leach et al., 2016; Fork et al., 2020; Xenopoulos et al., 2021; Morison et al., 2022). For example, it is largely unknown how drought events – which are expected to become more common in the boreal region as climate change progresses (IPCC, 2014; Büntgen et al., 2021) – influence the source, transport and transformation of DOM (Gómez-Gener et al., 2020; Gómez-Gener et al., 2021; Tiwari et al., 2022;

Wardinski et al., 2022). Research has focused more often on how climate change will influence downstream DOC concentration and load, rather than how it may influence the downstream DOM quality (Xenopoulos et al., 2021). Understanding the source and fate of DOM under a changing climate is also difficult because it is incorrect to assume that landscape sources of DOM will remain the same over time given the dependence of accumulation and transport of DOM on temperature and hydrology, in addition to the variability in landscape characteristics among boreal headwater catchments.

2.4.3 Research question and hypotheses

Here I ask how the terrestrial source of DOM influences the quantity and quality of DOM downstream in three boreal headwater catchments. Using historical streamflow and concentration data from IISD-ELA, as well as both DOM concentration and quality analysis on streamwater and water-extractable organic matter from 2021, I attempt to answer this question with three hypotheses:

H1: Concentration-discharge relationships vary between wet and dry years historically, and these relationships depend on catchment characteristics.

H2: DOM quantity and quality in soil leachate depends on both topography and soil organic matter content.

H3: Stream DOM concentration and quality depends on landscape sources of DOM, which are mediated by hydrological conditions.

3. Methods

3.1 Study Sites

This study was undertaken in the surrounding watersheds of headwater lake 239 (L239) at the IISD-ELA, in Northwestern Ontario, Canada. This reference lake has extensive long-term biogeochemical and hydrological data (1969-present) (Parker et al., 2009). The L239 watershed (3.3 km^2) comprises three small catchments which are drained by first-order streams (Schindler et al., 1996), and are 62-93% jack pine (*Pinus banksiana*) (Emmerton et al., 2019). These three catchments contain thin (<1m deep) orthic brunisolic soils overlain on pink Precambrian granodiorite (Brunskill & Schindler, 1971; Parker et al., 2009). None of the three catchments have been managed (e.g., logged, cultivated), but there have been major windstorms and fires which affected parts of the L239 watershed in the 1970s and 1980s (Emmerton et al., 2018). During the non-growing season (November – April), mean daily air temperatures range from -15.6 to +3.8°C, while during the growing season (May – October) temperatures range from +4.7 to 19.4°C (Emmerton et al., 2019). Mean annual precipitation is 705 mm and ~78% falls as rain (Emmerton et al., 2019).

The eastern catchment (EIF) has the largest area (1.7 km^2), as well as the highest mean elevation, highest mean slope, and lowest topographic wetness index (Supplemental Table 1). This catchment contains the longest stream and largest riparian area (Figure 1). The stream channel (~0.4 - 1 m wide) extends ~1 - 1.5 km from the L239 inflow (Parker et al., 2009). Additionally, an ephemeral stream connects and creates a fork in the stream ~400m from the lake at times where catchment wetness is higher (Bottomley, 1974). This narrow catchment is composed of 6% valley bottom, as well as primarily upland and riparian forests (80% of the catchment area) which are surrounded by clearly defined rock outcroppings (10% of the catchment area) (Schindler et al., 1996). This catchment also features a riparian wetland (~4% of the catchment area) which is located the furthest upstream of all three catchments. This catchment is referred to as the upland-large catchment.

The northwestern catchment (NWIF) has the second largest area (0.56 km^2), as well as the lowest mean slope and highest mean NDVI (Supplemental Table 1). This catchment contains a small stream which extends only ~0.1-0.2 km from the lake inflow (Parker et al., 2009). There is a small, forested wetland (~0.02 km^2, ~3.5% of the catchment area) near this stream at the bottom of the catchment (Schindler et al., 1996, Parker et al., 2009). Much like EIF, the NWIF catchment is heavily forested, however, this catchment is much flatter topographically. This catchment is referred to as the upland-small catchment.

The northeastern catchment (NEIF) has the smallest area (0.12 km^2), as well as the lowest mean elevation and highest mean topographic wetness index (Supplemental Table 1). This catchment also contains a small stream which extends only ~0.1-0.2 km^2, however, the gauged v-notch weir where streamflow and chemistry data is collected is located near the end of the stream furthest inland (Figure 1). This catchment is defined by a relatively large, sparsely treed, acidic *Sphagnum* bog which extends from the gauged weir inland (0.037 km^2, ~30% of the catchment area). The catchment area surrounding this peatland is much like the other two catchments in that it features shallow soils and dense, rocky, upland forests. However, the extent and proximity of the wetland to the stream outflow means that it is likely that whatever DOM reaches the stream is funneled through this large wetland during most hydrological conditions. This catchment is referred to as the wetland-dominated catchment.

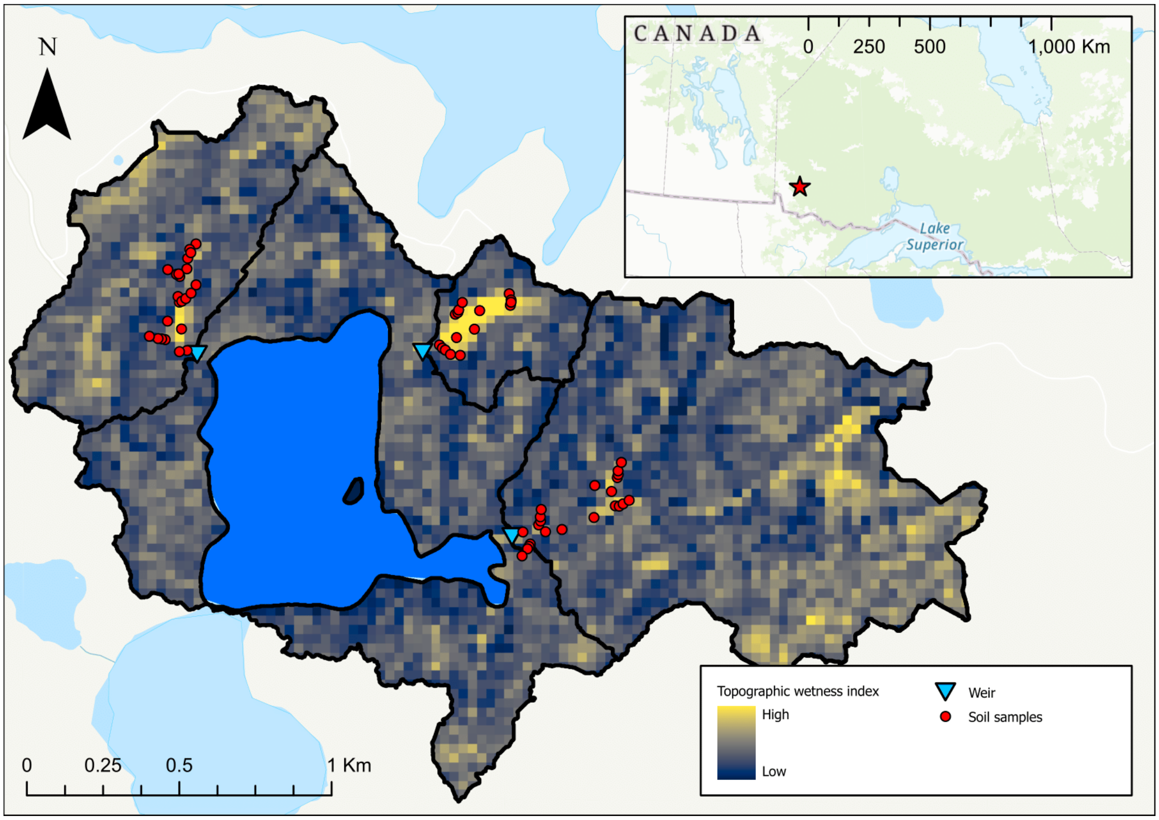


Figure 1: Site map showing the locations of soil samples juxtaposed on top of topographic wetness index for the three L239 catchments. Lake inflows where stream samples were taken are also labelled ("Weir").

3.2 Sampling Design

3.2.1 Streamwater samples

3.2.1.1 2021 sampling campaign

Streamwater samples were typically collected weekly throughout the 2021 from gauged v-notch weirs located near the lakeside edge of each catchment (Figure 1). The total number of samples collected from these streams was limited by the hydrological drought which occurred from approximately June 20 to October 8 (Figure 2). Stream samples were not collected when there was no flow crossing the threshold of the weir. There were 28 total stream samples taken from all streams throughout 2021. Streamwater samples were collected in polycarbonate bottles and were immediately refrigerated in the dark at 4°C.

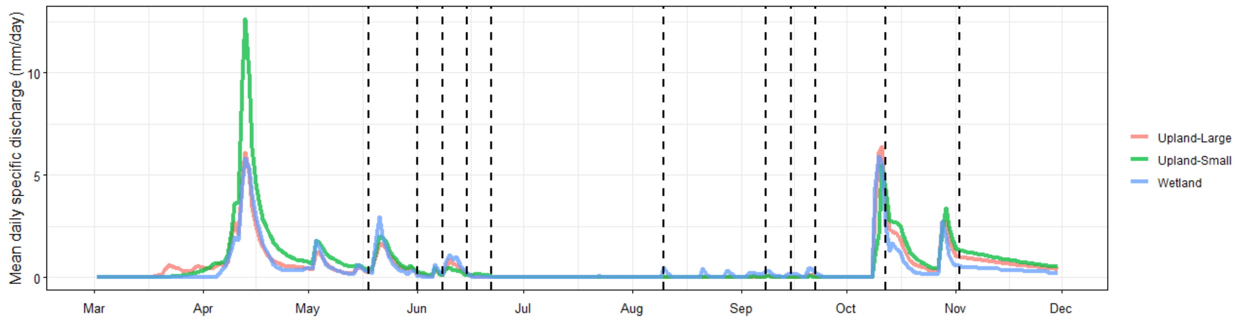


Figure 2: Time series of discharge for 2021 with sample points noted by dashed vertical lines.

3.2.1.2 Historical flow and chemistry data

Flow has been monitored continuously since 1971 at calibrated v-notch weirs draining each of the three catchments (Figure 1) using automated water level recorders (Beaty & Lyng, 1989). Mean daily specific discharge was calculated by dividing the flow data for each stream by the catchment area of each respective watershed. Water chemistry was also monitored weekly, except for non-flow conditions, from each of the streams at the site of the v-notch weirs (Figure 1) since 1971. Samples were transported in precleaned plastic bottles to the onsite laboratory at within a few hours of collection. DOC concentration was analyzed by filtering the samples through pre-combusted Whatman GF/C filters, acidifying the samples, stripping the samples of inorganic carbon, and digesting the samples either with acid persulfate (from 1971-1975), UV irradiation (from 1975-1985), or heating the samples to 102°C and measuring the infrared absorbance (1986 onwards) (Schindler et al., 1997). Only stream flow and chemistry data from 1981-2021 was used, as this was following the forest fire which burned most of the area around L239 in 1980 (Bayley et al., 1992).

Using the mean daily specific discharge across a given water year (e.g., Oct 1, 2020 – Sept 30, 2021), I quantified how dry or how wet a specific stream was in a given water year. If mean daily specific discharge was below quartile 1, the water year was considered dry. If mean daily specific discharge was between quartile 1 and 3, the water year was considered average. If mean daily specific discharge was above quartile 3, the water year was considered wet. The year 2021 was considered a dry water year in all three streams according to this classification (Figure 3). Average years are excluded from further analyses, so the focus is on comparing dry and wet years.

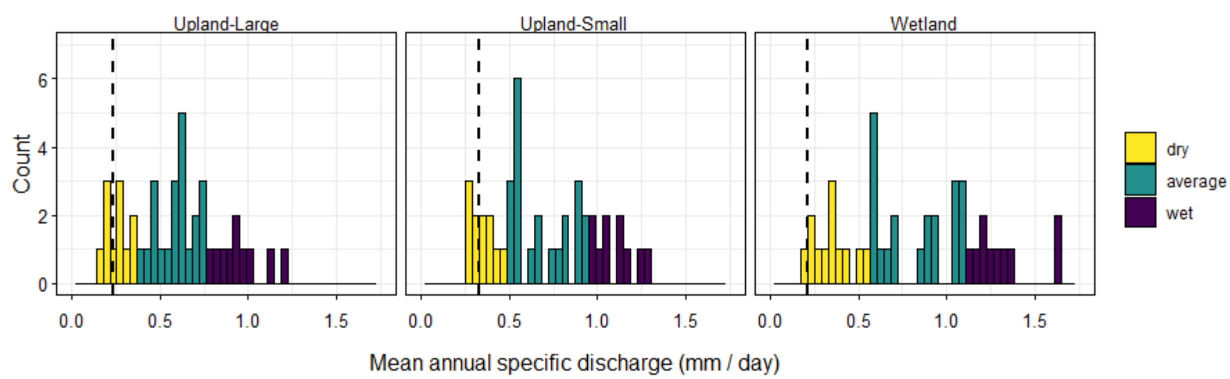


Figure 3: Mean annual specific discharge histograms for dry, average, and wet water years based on data from 1981-2021. 2021 was considered a dry year and is denoted by vertical dashed lines.

3.2.2 Soil samples

Throughout the three catchments, 60 total soil samples were collected in July of 2021 (Figure 1). At each location, an auger was used to collect three soil samples from 0-20 cm soil depth within a 1 metre radius and immediately combined into a composite soil sample. Sample location was limited by soil depth, as locations further upslope and further from the near-stream organic soils typically have soil depths less than 20 cm.

3.3 Analytical methods

3.3.1 Soil analysis

Composite soil samples were air-dried, sieved to <2mm, and homogenized via mortar and pestle prior to analysis. Soil organic matter was determined via loss-on-ignition (LOI) by measuring the loss in soil mass after placing 1 g of soil in a muffle furnace for 3 hours at 550°C (adapted from Hoogsteen et al., 2015). Soils with more than 20% organic matter content were considered organic and with less than 20% were considered mineral based on the Canadian Soil Classification (1998). Initial soil leachate was extracted by placing 2.5 g of soil into 100 ml of ultrapure water (1:40 soil to water ratio). The ratio was chosen such that the resulting DOC concentration was in the same range as observed lysimeter soil water concentrations (Friesen-Hughes, unpublished data). This mixture was then agitated on a horizontal shaker for 2 hours to enhance leaching. The mixture was then centrifuged at 5000g for 20 min to accelerate the subsequent filtration. Replicates were created every 1 in 20 samples by using a different subsample of soil from the same soil sample to create the leachate. Duplicates were also created every 1 in 20 samples by analyzing a second supernatant subsample from the same soil leachate. Soil leachate methodology was adapted from Guigue et al., (2014), Bertolet et al., (2018), Hensgens et al., (2020), and da Silva et al., (2021b).

3.3.2 Water chemistry analyses

All water samples (soil leachate and streamwater) were filtered through 0.45 µm polyethersulfone filters and refrigerated at 4°C in the dark in acid-washed polycarbonate bottles. After initial filtration, all water samples were analyzed for DOC and total dissolved nitrogen (TDN). DOC and TDN were measured simultaneously with a Shimadzu TOC-L CSN + TNM-L analyzer equipped with an ASI-L autosampler.

Each water sample was subsampled and filtered through 0.22 µm polycarbonate filters for optical analysis. DOM quality was determined using a Horiba Aqualog fluorescence spectrometer with a Fast-1 autosampler using a 1 cm quartz cuvette. Analysis of both absorbance and fluorescence spectroscopy data gives greater detail of the overall quality of DOM compared to using either individually (D’Andrilli et al., 2022). Water samples were kept in the dark at 4°C but allowed to warm to room temperature prior to being analyzed. UV absorbance spectra were measured from 220 to 600 nm at 5nm increments. Emission was measured in 5 nm increments from wavelengths 220 to 600 nm; excitation was measured in 2.33nm increments from 250 to 800 nm and interpolated to 5nm increments. Blank subtraction (using ultrapure water), inner-filter effect correction, Rayleigh masking, and Raman normalization were all part of the pre-processing for optical parameters. All optical parameters were calculated using the “staRdom” package (Pucher et al., 2019) for R (R Core Team, 2022).

3.3.2.1 Absorbance indices

Specific UV absorbance at 254 nm ($SUVA_{254,}$ L mg-C^{-1} m^{-1}) is calculated by dividing the absorbance coefficient at 254 nm by the DOC concentration (Weishaar et al., 2003). $SUVA_{254}$ is used as an indicator of the aromaticity of DOM, with higher values indicating higher aromaticity (Weishaar et al., 2003; Hur & Kim, 2009, Chen et al., 2011). Spectral slope ($S_{275-295}$) was calculated by determining the nonlinear fit of an exponential function from 275-295 nm of the absorption spectrum (Helms et al., 2008). $S_{275-295}$ is used as an indicator of the average molecular weight of DOM, with higher values indicating lower average molecular weight DOM (Helms et al., 2008). Spectral slope ratio (S_r) is calculated by dividing the $S_{275-295}$ by the spectral slope at 350-400nm and is negatively correlated with the molecular weight of DOM (Helms et al., 2008). Together, $SUVA_{254}$, $S_{275-295}$, and S_r tell us about the molecular composition of DOM and can help us in assessing potential changes in DOM quality which have repercussions for downstream waterbodies.

3.3.2.2 Fluorescence indices

BIX is used as an indicator for freshly-produced autochthonous (i.e., microbially-derived) DOM, with higher values corresponding to DOM more recently-produced autochthonous origin and lower values corresponding to older, more allochthonous (i.e., terrestrially-derived) origin (Huguet et al., 2009). The Biological index (BIX) was calculated by dividing the emission intensity at 380 nm by the emission intensity at 430 nm at an excitation spectrum of 310 nm (Huguet et al., 2009). Fluorescence index (FI) is defined as the ratio between emission intensities at 450-500nm at an excitation of 370 nm (McKnight et al., 2001). FI is used as an indicator for the terrestrial or microbial origin of fulvic acids in surface waters and is often related to aromaticity. Lower FI values indicate higher aromatic content and more terrestrial origins (McKnight et al., 2001; Cory & McKnight, 2005).

3.3.3 Data analysis

3.3.3.1 Concentration-discharge analysis

Water year (the 12-month period from October 1 of one year to September 30 of the next), was used to classify streams into quartiles where a water year average of streamflow below quartile 1 was considered a dry year, between quartile 1 and 3 was considered an average year, and above quartile 3 was considered a wet year. Concentration-discharge (c-Q) analysis was conducted on all stream data except for dates between October 1 and January 1. This way, c-Q relationships were assessed from the snowmelt period into the fall of one singular growing season. Concentration-discharge analysis was conducted by fitting linear regressions to log-transformed mean daily specific discharge and DOC and TDN concentration. This analysis was carried out from April 1 – Nov 30 each year from 1981-2021, as well as June 1 – Nov 30 for assessing the influence of snowmelt on annual concentration-discharge relationships. As mentioned above, this analysis was conducted on dry and wet water year growing seasons. Antecedent flow analysis was conducted by creating a rolling sum of daily flow data for the preceding 7, 14, 21, and 28 days.

3.3.3.2 Statistical analysis

Linear regression models were used to analyze relationships between DOM concentration, quality indices, flow, and antecedent flow. Relationships were considered significant at $p < 0.05$. Spearman correlation coefficients were calculated to analyze the relationship between spatial variables (e.g., slope) and principal component values (see below). Kruskal-Wallis tests were used to determine if significant differences existed among catchments for DOM quantity and quality in the form of principal component values in soil leachate (where $p < 0.05$ means there is a significant difference).

Principal component analysis (PCA) was used to characterize the relationship among DOM concentration (DOC, TDN) and quality ($SUVA_{254}$, $S_{275-295}$, S_r, BIX, FI) variables in soil leachate and streamwater samples. PCA extracts components to explain variance among groups of variables loaded onto different axes. Each principal component axis is independent and uncorrelated from one another. PCA was used to summarize relationships among variables and also used to extract components to be used as response variables to hydrological predictors. Positive and negative loadings on components 1 or 2 were only discussed where loadings were greater than 0.4. All statistical analysis were performed using R 4.2.2 (R Core Team, 2022).

4. Results

4.1 Stream chemistry

The DOC concentrations in the study streams during the 2021 water year fell within the range of the historical data from each respective stream (Supplemental Figure 1). The wetland-dominated stream had the highest DOC concentration (historical mean = 41.87 mg/L; 2021 mean = 52.99 mg/L), whereas the two upland-dominated streams had much lower DOC concentrations (EIF: historical mean = 23.29 mg/L, 2021 mean = 18.60 mg/L; NWIF: historical mean = 20.40 mg/L, 2021 mean = 19.76 mg/L) (Supplemental Table 2). In 2021, the DOC concentration was above average in the wetland-dominated stream and below average in the upland-dominated streams.

4.2 Concentration-discharge relationships

4.2.1 Daily c-Q relationships in dry and wet water years

In dry water years, DOC concentration (c) was significantly correlated with mean daily specific discharge (Q) within all three streams (Figure 4). However, the strength and direction of these relationships varied among streams. For both of the upland-dominated streams, the slope of the c-Q relationship was slightly positive (EIF: slope = 0.046, $r^2 = 0.079$, $p < 0.05$, NWIF: slope = 0.033, $r^2 = 0.032$, $p < 0.05$), indicating that DOC became mobilized to streams at high flow (Figure 4, Supplemental Table 3), whereas in the wetland-dominated stream, the slope of the c-Q relationship was negative (slope = -0.054, $r^2 = 0.086$, $p < 0.05$), indicating that streamwater DOC became diluted during high flow in dry years (Figure 4, Supplemental Table 3).

In contrast to dry years, the c-Q relationships of the two upland-dominated streams were negative during wet years (EIF: slope = -0.024, r^2 = 0.018, $p < 0.05$; NWIF: slope = -0.035, r^2 = 0.039, $p < 0.05$), indicating a switch from transport-limitation in dry years to source-limitation in wet years (Figure 4, Supplemental Table 3). In the wetland-dominated stream, the slope of the c-Q relationship was even more negative in wet years compared to dry years (slope = -0.081), indicating that dilution of DOC in this stream increased in wet years, and that DOC in this stream is source-limited regardless of how wet the year was overall (Figure 4, Supplemental Table 3).

Analyzing c-Q relationships during (April 1 – May 31) and after (June 1 – Nov 30) the snowmelt period revealed how this period potentially influenced annual c-Q relationships (Supplemental Table 4). In dry years during the snowmelt period, c-Q relationships were positive in the upland-dominated streams (EIF: $p < 0.05$, r^2 = 0.098, slope = 0.048; NWIF: $p < 0.05$, r^2 = 0.246, slope = 0.096). While in wet years during the snowmelt period, c-Q relationships were more negative in the upland-dominated streams (EIF: $p > 0.05$, r^2 = 0.002, slope = -0.007; NWIF: $p > 0.05$, r^2 = 0.039, slope = 0.030). Whereas in the wetland-dominated stream, the c-Q relationship was negative in dry years ($p < 0.05$, r^2 = 0.319, slope = -0.110) and even more negative in wet years ($p < 0.05$, r^2 = 0.467, slope = -0.165).

After the snowmelt period (June 1 – Nov 30), the c-Q relationships were often different than during the snowmelt period (Supplemental Table 5). Among the upland-dominated streams, there were different c-Q patterns in the post-snowmelt period. In the upland-large stream, the c-Q relationship was positive in dry years (EIF: $p < 0.05$, r^2 = 0.175, slope = 0.073) and slightly less positive in wet years (EIF: $p < 0.05$, r^2 = 0.034, slope = 0.030). Whereas in the upland-small stream, c-Q relationships were approximately flat in dry (NWIF: $p > 0.05$, $r^2 = 0.001$, slope = 0.005) and wet years (NWIF: $p < 0.05$, $r^2 = 0.003$, slope = -0.009). Concentration-discharge relationships were still negative in the wetland-dominated stream, but less so than during the snowmelt period, and not distinctly different among dry ($p < 0.05$, $r^2 = 0.023$, slope = -0.025) and wet years ($p < 0.05$, $r^2 = 0.020$, slope = -0.029).

In summary, this indicates that streams draining upland-dominated catchments tend to have c-Q relationships that are more transport-limited in dry years, and more source-limited in wetter years. Whereas the stream draining the wetland-dominated catchment experiences source-limitation regardless of the hydrological conditions of a given water year. Additionally, the snowmelt period tended to substantially influence annual c-Q relationships, being strongly negative in the wetland-dominated stream and positive in the upland-dominated streams. In the post-snowmelt growing seasons, c-Q relationships were less variable between dry and wet years, and the direction of these relationships was distinct among all three streams.

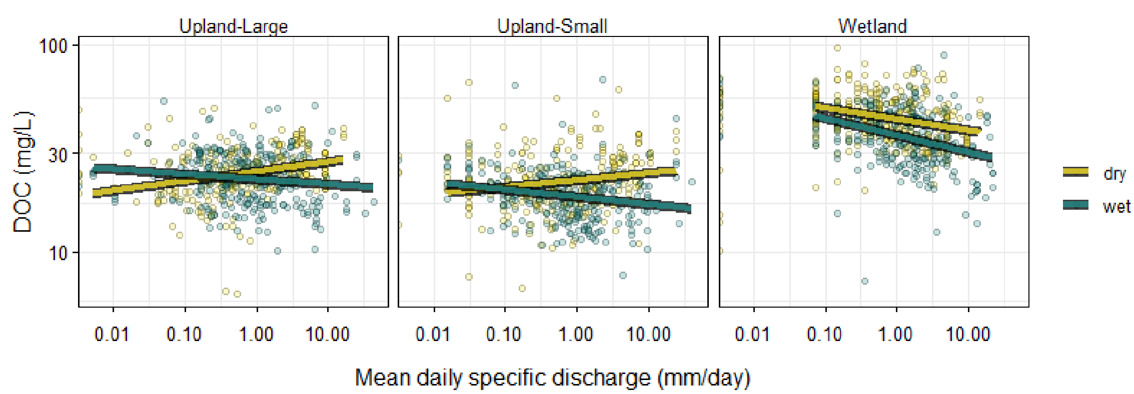


Figure 4: Concentration-discharge relationships in each stream for DOC concentration during dry and wet water years from April 1 – Nov 30. All linear regression model fits were significant ($p < 0.05$).

4.2.2 Does antecedent flow improve c-Q relationships in dry and wet water years?

In some cases, antecedent flow (AQ) was a better predictor of DOC concentration than mean daily specific discharge. In the upland-dominated streams, daily flow was a better predictor than 7-day, 14-day, 21-day, or 28-day AQ of DOC concentration in dry years (Supplemental Table 6). However, 21-day AQ was a better predictor of DOC concentration in the upland-dominated streams (EIF: $p < 0.05$, $r^2 = 0.048$, slope = -0.055; NWIF: $p < 0.05$, $r^2 = 0.179$, slope = -0.086) streams during wet years (Supplemental Table 6). In the wetland-dominated stream, AQ was a better predictor of DOC concentration in both dry (14-day AQ: $p < 0.05$, $r^2 = 0.337$, slope = -0.103) and wet years (28-day: $p < 0.05$, $r^2 = 0.339$, slope = -0.175) (Supplemental Table 6). During the dry snowmelt periods, daily flow was again the best predictor of DOC concentration in the upland-dominated streams. The best predictor of DOC concentration in wet years in the upland-dominated streams was either 21-day AQ (EIF) or was not significant in either daily Q or AQ (NWIF). In the wetland-dominated stream, 14-day AQ was the best predictor of DOC concentration in dry years during snowmelt ($p < 0.05$, $r^2 = 0.640$, slope = -0.137) and wet year snowmelts ($p < 0.05$, $r^2 = 0.620$, slope = -0.182) (Supplemental Table 7). In the post-snowmelt period, daily flow was the best predictor of DOC concentration in the EIF in both dry and wet years. However, 28-day AQ was the best predictor of DOC concentration in both the NEIF and NWIF streams in both dry (NEIF: $p < 0.05$, $r^2 = 0.278$, slope = -0.091; NWIF: $p < 0.05$, $r^2 = 0.153$, slope = -0.087) and wet years (NEIF: $p < 0.05$, $r^2 = 0.254$, slope = -0.150; NWIF: $p < 0.05$, $r^2 = 0.157$, slope = -0.078) (Supplemental Table 8).

4.3 Patterns of DOM concentration and quality in soil leachate

Using the DOM quality analysis conducted on 2021 water samples, I sought to better understand the historical c-Q relationships. Inferences of landscape source from streamwater DOM quality can be strengthened by also measuring the DOM quantity and quality among specific landscape sources among these boreal headwater catchments. To do so, soil properties (loss-on-ignition [LOI]) and spatial characteristics (slope and topographic wetness index [TWI]) were compared to the quantity and quality of DOM in soil leachate.

4.3.1 Principal component analysis of DOM concentration and quality in soil leachate

In soil leachate, the PCA of the 7 DOM quantity and quality variables explained 77.4% of the variance using 2 principal components, with 56.6% of the variance explained by component 1 and 20.8% of the variance explained by component 2 (Figure 5). Positive loadings on component 1 correspond to higher DOC, higher $SUVA_{254}$, lower $S_{275\text{-}295}$, and lower S_r. Positive loadings on component 2 correspond to lower TDN, lower BIX, and lower FI. Soil samples were well separated along both component 1 and component 2, with organic soils (soils with >= 20% LOI) have significantly higher mean component 1 and significantly lower component 2 scores ($p < 0.05$ in both cases, according to a Kruskal-Wallis test). The mean, SD, min, and max of each individual metric can be found in Supplemental Table 9.

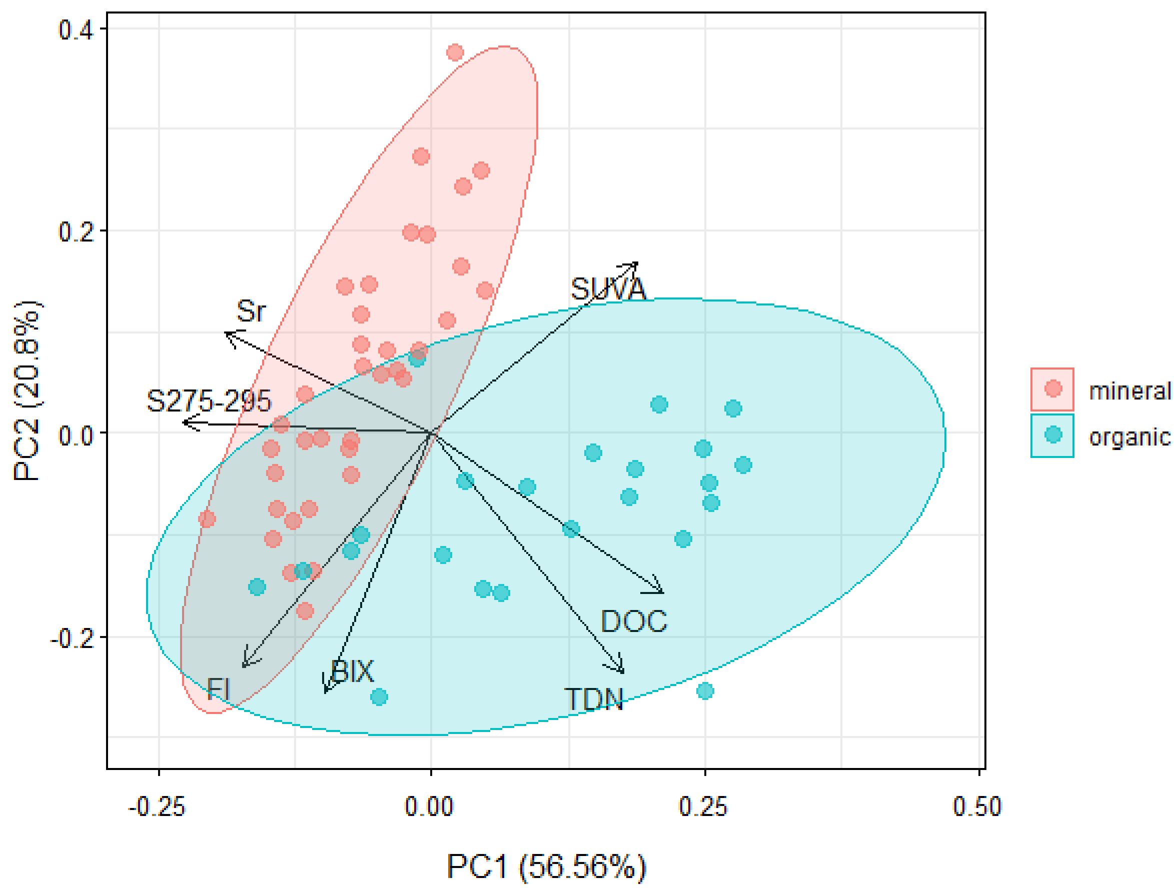


Figure 5: Principal component analysis (PCA) for DOC concentration, TDN concentration and DOM quality (SUVA254, S275-295, Sr, FI, BIX) variables in soil leachate separated by organic matter content (LOI >= 20% = organic, LOI < 20% = mineral).

4.3.2 Using spatial characteristics to predict soil leachate DOM quantity and quality

Component 1 and component 2 are dependent on the soil properties and spatial characteristics at each site (Figure 6). There are significant positive correlations between LOI and both component 1 ($p < 0.05$, coefficient = 0.578) and component 2 ($p < 0.05$, coefficient = -0.519) (Figure 6). There are significant correlations between slope and both component 1 ($p < 0.05$, estimate coefficient = -0.283) and component 2 ($p < 0.05$, coefficient = 0.515) (Figure 6). There are also significant correlations between topographic wetness index and component 1 ($p < 0.05$, coefficient = 0.430) and component 2 ($p < 0.05$, coefficient = -0.342) (Figure 6). Taken together, these results indicated that soil in wet locations in topographic depressions that are high in soil organic matter content tend to have soil leachate with higher DOC and TDN concentrations, as well as DOM quality that is more aromatic and of higher average molecular weight (as indicated by higher $SUVA_{254}$ and lower $S_{275\text{-}295}$ and lower S_r), as well as more recently produced (as indicated by higher FI and BIX).

When grouping each location into mineral (<20% LOI) and organic (>=20% LOI), it can also be seen that there are substantial differences among these two soil types (Figure 6). In fact, upon conducting the same analysis as above after splitting the data in this manner, it is clear that correlations between spatial indices and DOM indices (e.g., components 1 and 2) are driven heavily by soil groupings. Organic soil leachate was significantly higher than mineral soil leachate along component 1 and significantly lower than mineral soil leachate along component 2 ($p < 0.05$ in both cases, according to a Kruskal-Wallis test).

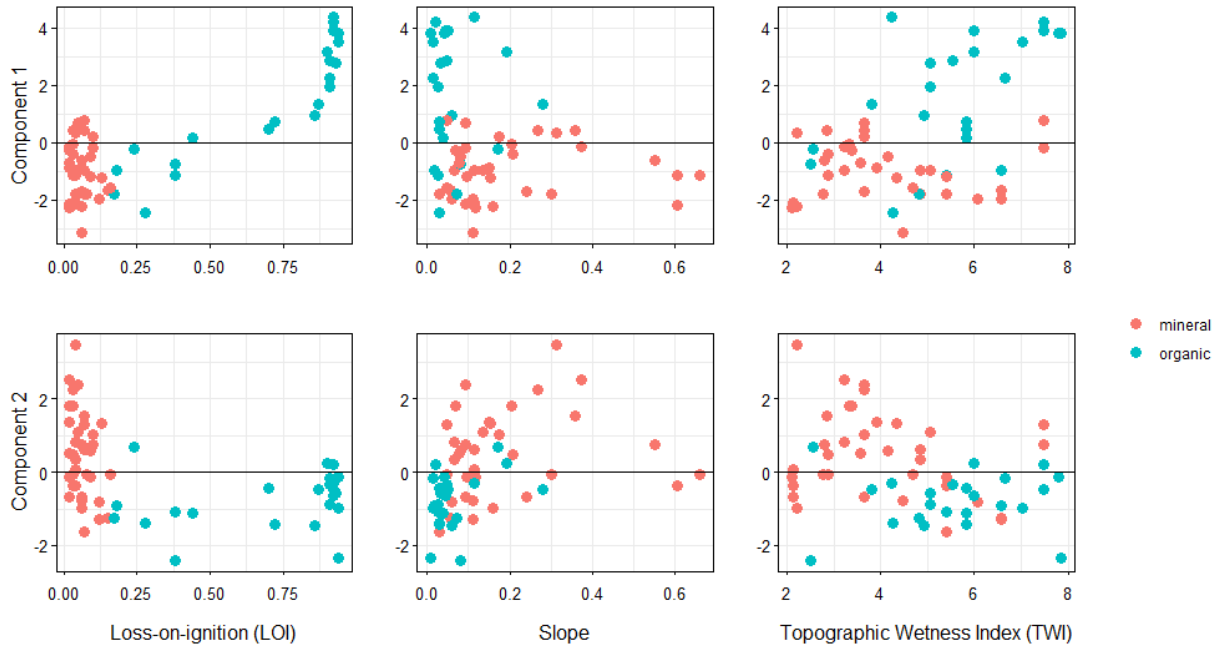


Figure 6: Scatterplots of principal components 1 (positive loadings = DOC; negative loadings = S275-295) and 2 (negative loadings: BIX, FI, TDN) and LOI, slope, and TWI, separated by whether LOI was >= 20% (organic) or < 20% (mineral).

4.4 Using specific discharge to predict DOM quantity and quality in streamwater in 2021

4.4.1 Concentration-discharge and DOM quality-discharge relationships in 2021

In streamwater, the PCA of the 7 DOM quantity and quality variables explained 80.5% of the variance using 2 principal components, with 51.6% of the variance explained by component 1 and 29.0% of the variance explained by component 2 (Figure 7). Positive loadings on component 1 correspond primarily to lower $S_{275-295}$, lower S_r, and lower FI. Positive loadings on component 2 correspond to higher DOC, higher TDN, and lower $SUVA_{254}$. The three catchments were clearly separated along components 1, and not as clearly separated along component 2. In particular, the DOM in the wetland-dominated stream had clearly higher component 1 values than the upland-dominated streams. Along component 2, the DOM among all three streams was very similar, however the upland-large stream (EIF) had a smaller and lower range of component 2 values. The mean, SD, min, and max of each individual metric can be found in Supplemental Table 10.

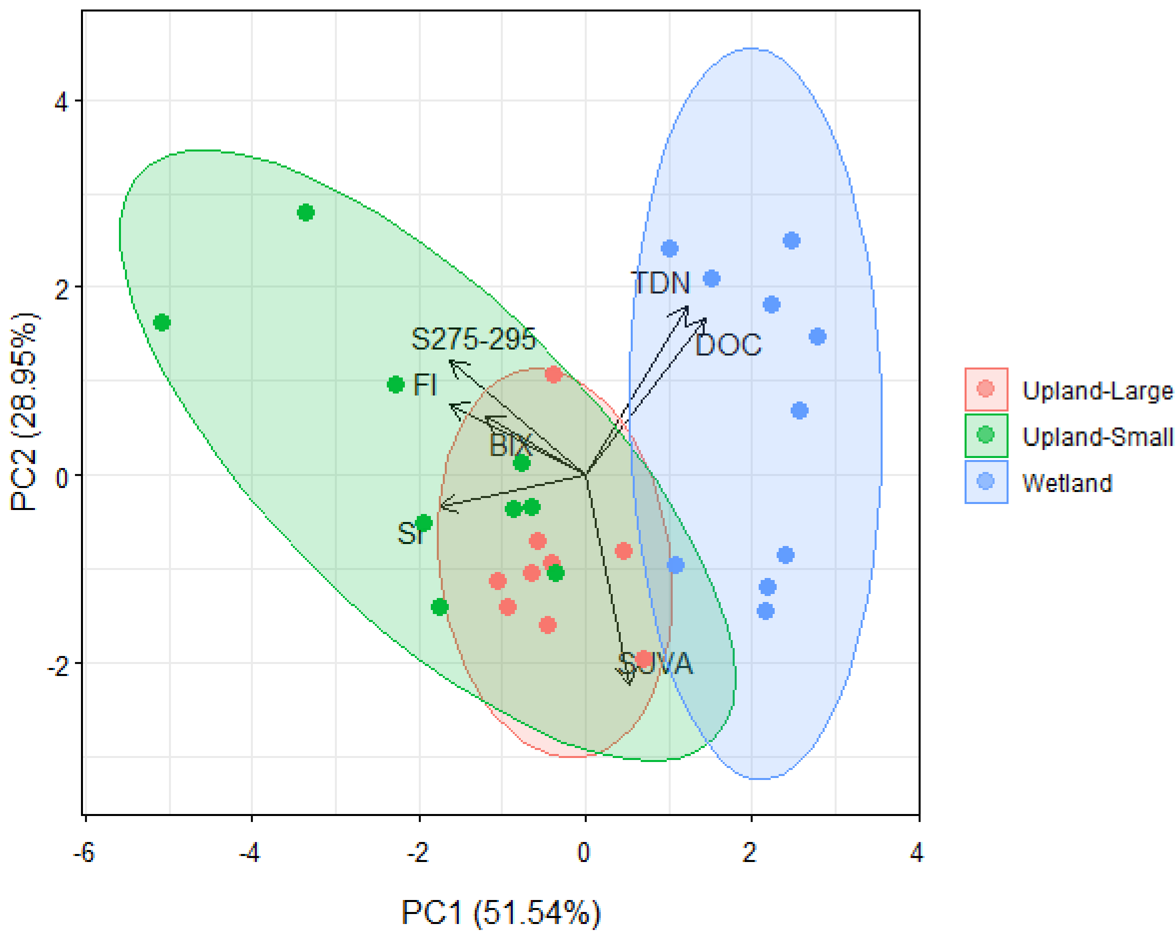


Figure 7: Principal component analysis (PCA) for DOC concentration, TDN concentration and DOM quality (SUVA254, S275-295, Sr, FI, BIX) variables in 2021 streamwater colored by stream.

4.4.2 DOM concentration and quality vs. daily flow in 2021

Many DOM concentration and quality indices depended on specific discharge, but the strength and direction of these relationships varied among indices. During the 2021 growing season, the c-Q relationship in the upland-large stream was slightly positive (Figure 8), which is consistent with the historically positive c-Q relationship in this stream in dry water years from June 1 – Nov 30 (Figure 4). In the upland-large stream, the c-Q relationship was approximately flat prior to the post-drought flush; after this flush, DOC concentration increased with increasing flow (being highest immediately post-drought and almost returning to baseline three weeks later) (Figure 8). The c-Q relationship in the upland-small stream was flat (Figure 8), which was expected given the historically flat c-Q relationship in this stream in dry water years from June 1 – Nov 30 (Figure 4). In the upland-small stream, the c-Q relationship was diluting prior to the post-drought flush; after this flush, DOC concentration increasing with increasing flow (being highest immediately post-drought and returning to baseline 3 weeks later) (Figure 8). During the 2021 growing season, the c-Q relationship in the wetland-dominated stream was flat (Figure 8), which was expected given the historically flat c-Q relationship in this stream in dry water years from June 1 – Nov 30 (Figure 4). In the wetland-dominated stream, the DOC concentration was substantially different from the pre-drought (mean = 37.4 mg/L) to the drought samples (mean = 41.9 mg/L) (Figure 8). As well, DOC concentration was slightly diluted post-drought compared to during the drought. DOC concentration and TDN concentration in each individual stream were highly correlated in 2021 ($p < 0.05$), and TDN concentration followed the same exact patterns in these streams (Supplemental Figure 4).

The $SUVA_{254}$-Q relationship in both of the upland-dominated streams was flat during the drought, and experienced a decrease after this event, with the lowest $SUVA_{254}$ (and thus, least aromatic DOM) coming immediately after the post-drought flush (Oct 12). In the upland-large stream, $SUVA_{254}$ returned towards the pre-flush mean by November 2, however, in the upland-small stream the $SUVA_{254}$ was still lower than the pre-flush mean at this time. In the wetland-dominated stream, $SUVA_{254}$ decreased with flow prior to the post-drought flush, and after this flush the $SUVA_{254}$ was distinctly lower than the rest of the growing season (with the exception of 2021-09-22), even 3 weeks post-flush (Nov 2). The $S_{275\text{-}295}$-Q relationship was in many ways very similar to the $SUVA_{254}$-Q relationship in these streams. Both of the upland-dominated streams had flat $S_{275\text{-}295}$-Q relationships during the drought and experienced an increase immediately after the post-drought flush (and thus, had the lowest average molecular weight during this time). Much like the $SUVA_{254}$, $S_{275\text{-}295}$ returned towards the pre-flush mean in the upland-large stream but not in the upland-small stream by November 2. In the wetland-dominated stream, $S_{275\text{-}295}$ increased with flow throughout the entire growing season (indicating decreasing average molecular weight with increasing flow). The FI-Q relationship in the upland-large stream was negative prior to the post-drought flush (with the exception of the June 1 stream sample) and positive after. The FI-Q relationships in both the wetland-dominated and upland-small streams were flat prior the post-drought flush (with the exception of the June 1 stream sample) and positive after as well. In all three streams, the highest FI value is immediately post-drought (Oct 12) but returned to the mean three weeks later (Nov 2). In the upland-large stream, there were significant linear relationships between flow and DOC ($p < 0.05$, $r^2 = 0.629$, slope = 0.144, based on log10 DOC and Q) and TDN concentrations ($p < 0.05$, $r^2 = 0.481$, slope = -0.229, based on log10 TDN and Q). In the wetland-dominated stream, there were significant relationships between $SUVA_{254}$ ($p < 0.05$, $r^2 = 0.540$, slope = -0.303, based on $SUVA_{254}$ and log10 Q), $S_{275\text{-}295}$ ($p < 0.05$, $r^2 = 0.542$, slope = 0.001, based on $S_{275\text{-}295}$ and log10 Q) and FI ($p < 0.05$, $r^2 = 0.456$, slope = 0.038, based on FI and log10 Q). No significant relationships were detected between daily flow components and principal components 1 and 2.

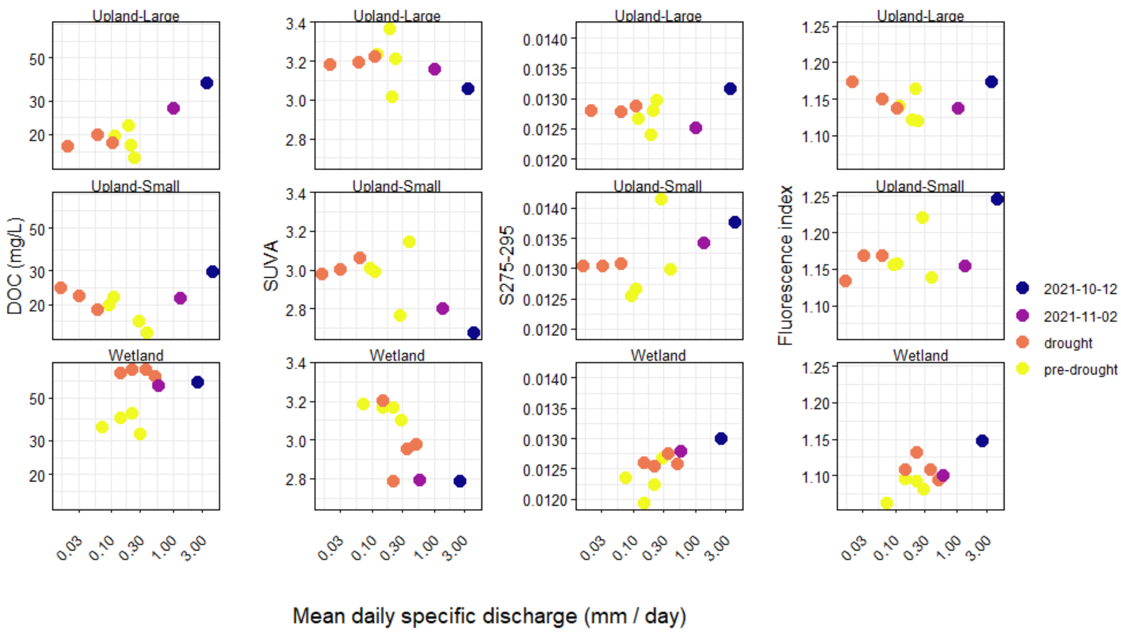


Figure 8: Relationships between flow and DOM concentration and quality. Data is separated into pre-drought, drought, and the two post-drought sample points (2021-10-12 and 2021-11-02).

5. Discussion

Historical data from three proximal headwater streams demonstrates that DOM c-Q relationships vary between wet and dry years and that these differences reflected the characteristics of each respective headwater catchment. Streams draining catchments with lower proportions of wetlands had more positive c-Q relationships during dry years that shifted to negative relationships during wet years, while a stream draining a wetland-dominated catchment had negative c-Q relationships in both dry and wet years. In order to further understand the mechanisms behind these historical c-Q patterns, I investigated the DOM quality in both streamwater and soil water during a year with a mid-summer drought. I found that DOM concentration and quality in soil leachate depends on the soil type (i.e. organic or mineral), which is largely driven by topography. Specifically, that organic soil leachate contained DOM which had a higher concentration of DOC, was more aromatic and higher average molecular weight compared to mineral soil leachate. Additionally, that organic soils were located in flatter locations with higher TWI. I found that stream DOM concentration and quality were substantially different post-drought compared to pre-drought. DOM was more concentrated, less aromatic, and of lower average molecular weight in the post-drought stream samples compared to pre-drought across all three streams. This indicates that as different parts of these catchments become hydrologically connected and subsequently flushed, the DOM quality in receiving streamwater changes. The monitoring data gives us insight into both the historically observed c-Q relationships as well as it helps us further understand what stream DOM dynamics in boreal headwater streams may look like in the future under changing drought regimes.

5.1 Long-term stream concentration-discharge relationships depend on catchment characteristics and hydrological conditions

Understanding c-Q relationships in headwater streams can inform us as to whether stream DOM dynamics are driven more by the spatial arrangement of landscape sources of DOM or the hydrological connectivity between those sources and the stream (Thompson et al., 2011; Creed et al., 2015; Moatar et al., 2017). As DOM concentrations in streams respond to changes in flow and wetness differently among these three streams historically, it follows that either the landscape sources of DOM and the ability of those sources to become connected to the stream must differ among catchments according to their landscape characteristics.

5.1.1 Wetlands

The presence and extent of wetlands in a catchment is a dominant driver of DOM quantity and quality in streams (Dillon & Molot, 1997; Hinton et al., 1998; Aitkenhead et al., 1999; Creed et al., 2003; Mulholland, 2003; Laudon et al., 2004; Ågren et al., 2007; Creed et al., 2008; Laudon et al., 2012; Walker et al., 2012; Winterdahl et al., 2014; Dick et al., 2015; Hytteborn et al., 2015; Monteith et al., 2015; Tiwari et al., 2017; Zarnetske et al., 2018; Casson et al., 2019). Streams draining wetland-dominated catchments experience dilution of DOM at high flow (Schiff et al., 1998; Laudon et al., 2004; Laudon et al., 2011; Peralta-Tapia et al., 2014; Birkel et al., 2017; Ducharme et al., 2021), and this was observed in the wetland-dominated stream. Streams draining wetland-dominated catchments tend to experience less fluctuations in DOC concentration with hydrological change (Schiff et al., 1998); this was observed in the wetland-dominated stream, where c-Q relationships remained negative regardless of time period observed (growing season, snowmelt, post-snowmelt) or water year wetness. This has been attributed to the fact that wetlands have intrinsically high water tables and thus, hydrological additions do not substantially alter hydrological connectivity with organic-rich subsurface peat horizons (Schiff et al., 1998). Snowmelt tends to cause dilution of DOM in stream draining wetland-dominated catchments (Buffam et al., 2007; Laudon & Buffam, 2008; Ågren et al., 2008a; Eimers et al., 2008; Laudon et al., 2011), which matches the c-Q relationships observed during and after the snowmelt period in the wetland-dominated stream. The post-snowmelt c-Q relationships were very similar among dry and wet years in the wetland-dominated stream which highlights the resilience to hydrological change in stream DOM dynamics that wetlands provide and the dominance of source-limitation in streams draining wetland-dominated catchments (Schiff et al., 1998; Laudon et al., 2004; Laudon et al., 2011; Peralta-Tapia et al., 2014; Birkel et al., 2017; Ducharme et al., 2021).

Dry conditions affect the influence of wetlands on stream DOM either through changes to hydrology via water table drawdown (Strack et al., 2008; Jager et al., 2009), or biogeochemistry via enhanced redox of peat causing carbon mineralization and processing of organic matter (Moore & Dalva, 1993; Kalbitz et al., 2000; Freeman et al., 2001; Sippel et al., 2018). Dry conditions enable wetlands to have greater capacities to absorb hydrological additions and delay stream response in comparison to wet conditions (Lane et al., 2020) which explains why the c-Q relationship in the wetland-dominated stream was less negative in dry years compared to wet years. The delayed response in streamwater to hydrological additions in wetland-dominated landscapes (Lane et al., 2020) also helps explain why antecedent flow was a better predictor than daily flow of streamwater DOC concentrations and provides context for previous research showing how antecedent wetness controls stream DOC concentrations (Raymond & Saiers, 2010; Oswald & Branfireun, 2014 Tunaley et al., 2016). Only when analyzing the driest 5% of years (i.e. years where annual flow is below the 5th quantile based on the historical record) did I see the c-Q relationship in the wetland-dominated stream switch from negative to positive ($p < 0.05$, estimate = 0.391). This illustrates that under severe drought conditions, wetlands may become disconnected from streams in a substantial way, either due to water table drawdown from upper peat layers (Jager et al., 2009) or laterally disconnected pools of wetland DOM (Schiff et al., 1998).

Dry conditions create lower water tables, a condition which has been shown to both increase (Tipping et al., 1999; Worrall et al., 2004) and decrease stream DOM concentrations (McLaughlin et al., 1994; Clark et al., 2005; McLaughlin & Webster, 2010). This is likely due to the unique and changing influence of two interacting controls: hydrology and biogeochemistry. Dry conditions have lower hydrological connectivity between streams and wetlands, as well as more aerobic conditions favouring enhanced microbial processing and decomposition of soil DOM (Moore & Dalva, 1993; Fang & Moncrieff, 2001; Freeman et al., 2001; Bertolet et al., 2018), both of which potentially reduce the amount of DOM reaching streams. While drier conditions reduce loads of DOM to streams, the inherently lower streamflow levels mean that resulting stream DOM may be more concentrated than under wetter conditions. This difference between load and concentration is well-illustrated in the wetland-dominated stream, where in the post-snowmelt growing season, historical c-Q relationships are the same directionally among dry and wet years.

5.1.2 Riparian zones

The presence and extent of riparian zones is a critical control on stream DOM concentrations in headwater streams (Fiebig et al., 1990; Bishop et al., 1994; Grabs et al., 2012; Knorr, 2013; Ledesma et al., 2015; Musolff et al., 2018). Like wetlands, riparian soils also accumulate large stores of organic matter (Grabs et al., 2012; Strohmeier et al., 2013; Ledesma et al., 2015; Ledesma et al., 2018a; Musolff et al., 2018; Ploum et al., 2020), however, riparian zones have a different influence on stream DOM dynamics due to differences in hydrology and biogeochemistry. Hydrologically, riparian zones experience greater variability in water table level than wetlands (Singh et al., 2014; Broder et al., 2017) and riparian soils feature the transmissivity feedback mechanism where hydrological additions raise the water table to surface soil horizons where lateral hydraulic conductivity is higher which favours rapid flushing of DOM to streams (Bishop et al., 2004; Bishop et al., 2011; Ledesma et al., 2018b). Biogeochemically, more variable redox conditions change processing of riparian DOM, thus altering both the quantity and quality of DOM available to streams (Singh et al., 2014; Broder et al., 2017). Streams draining catchments with extensive riparian areas tend to experience mobilization at high flow (Broder et al., 2017; Ledesma et al., 2018a; Fork et al., 2020), especially after drier conditions (Raymond & Saiers, 2010; Broder et al., 2017; Bernal et al., 2019), and this was also observed in the upland-large stream regardless of time period observed (i.e., during snowmelt, post-snowmelt, or the entire growing season).

One cause of transport-limitation in dry years in streams draining catchments with extensive riparian zones is that as water tables rise, flowpaths intersect with organic-rich shallow soil horizons (e.g., vertically in the riparian zone), creating a flush of DOM to streams (Bishop et al., 1990; Laudon & Slaymaker, 1997; Schiff et al., 1998; Sanderman et al., 2009; Tiwari et al., 2014; Ledesma et al., 2015). Another cause may be that under drought conditions, upper reaches of streams may dry up, resulting in the upstream riparian pools of DOM becoming disconnected, until conditions wet up and these pools become sources of DOM flushed to streams (Blaurock et al., 2021). Though water table drawdown occurs in both wetlands and riparian zones, wetlands are more consistent contributors to stream DOM under more variable hydrological scenarios. This is because the ability of riparian zones to contribute to stream DOM depends on water table level and whether or not organic-rich near-surface soil horizons are being flushed or not (Hinton et al., 1998; Seibert et al., 2009; Laudon et al., 2011; Winterdahl et al., 2011). Dry conditions cause riparian zones to detach from streams as sources of DOM due to water table drawdown, whereas wetlands remain sources of DOM up until more extreme drought conditions are met. This conceptual framework helps us understand why c-Q relationships varied more in the upland-large stream compared to the wetland-dominated stream.

5.1.3 Uplands

In streams draining catchments with lower proportions of wetlands, proportionally more organic matter comes from mineral soils, although this proportion depends on both hydrological conditions and the presence and location of organic soils (McGlynn & McDonnell, 2003; Godsey et al., 2009; Herndon et al., 2015). These streams tend to have positive c-Q relationships (Hinton et al., 1997; Hinton et al., 1998; Schiff et al., 1998; Wiegner et al., 2009; Raymond & Saiers, 2010; Bass et al., 2011; Laudon et al., 2011; Dhillon & Inamdar, 2014; Ducharme et al., 2021), which in snowmelt-dominated systems can be the result of high concentrations of DOC being flushed during the spring freshet (Hornberger et al., 1994; Hinton et al., 1997; Ågren et al., 2010). In the present study, c-Q relationships were always positive in drier years at the upland-dominated catchments but became less positive and sometimes negative during wetter years. This moisture-related shift in c-Q relationship direction shows that upland-dominated streams are more likely to become disconnected from landscape sources of DOM (e.g., riparian zones and riparian wetlands) under drier conditions. Forest soils display greater vertical variation in soil solution DOM compared with wetlands, which explains the higher DOM sensitivity to flow observed in upland-dominated catchments compared with the wetland-dominated catchment (Winterdahl et al., 2016). The switch to more source-limitation under wetter conditions indicates that as hydrological connectivity increases in upland-dominated catchments, the signal of DOM from near-stream organic sources is attenuated by more distal mineral soils (Laudon et al., 2011; Wen et al., 2020). As well, I found that c-Q relationships were much more positive in dry years during the snowmelt period compared with wetter years in both upland-dominated catchments. This suggests that autumn and winter stores of landscape DOM becomes more diluted during snowmelt in upland-dominated streams in dry years compared to wet years.

Relatively small wetlands can be important sources of DOM to streamwater (Hamond, 1990; Hinton et al., 1998) especially riparian wetlands (Inamdar et al., 2012; Strohmeier et al., 2013) located in flatter catchments (Creed & Band, 1998; Creed et al., 2003). This influence was observed in the flattest catchment which had a low proportion of wetlands, little riparian extent, but a small near-stream wetland. While previous research has shown that the overall wetland proportion is a better predictor than near-stream riparian proportion (Casson et al., 2019), the two upland-dominated streams differed in c-Q relationships post-snowmelt perhaps as a result of the difference in the location of their wetlands. The upland-large catchment has a wetland further upstream past the riparian zone, while the upland-small catchment has a small wetland adjacent to the stream outlet. The catchment with the near-stream wetland had less variable c-Q relationships of streamwater between dry and wet years compared with the catchment with a distal wetland. This suggests that the near-stream wetland is a more consistent source of DOM to streamwater than the far-stream wetland, though the difference in riparian extent and slope among these two catchments makes the influence of wetland proximity difficult to isolate. I found that mean daily specific discharge was a better predictor of DOC concentration in dry years whereas antecedent flow was a better predictor of DOC concentration in wet years in the upland-dominated streams. This may be caused by the enhanced DOM accumulation in riparian zones under dry conditions which can be quickly mobilized with hydrological additions, whereas in wet years, where riparian water tables are higher, catchment wetness - which antecedent flow is an indicator of – must increase sufficiently so as to substantially alter the supply of both water and DOM to streams (Tunaley et al., 2016).

5.2 Stream DOM concentration and quality depends on both landscape source and hydrological connectivity

Topography exerts a primary control over soil formation, which includes the accumulation of organic matter across the landscape. Stream DOM dynamics depend on the slope (Eckhardt and Moore, 1990; D’Arcy and Carignan, 1997; Hazlett et al., 2008) and area (Mulholland, 1997; France et al., 2000; Ågren et al., 2007) of a given catchment, both of which couple with other topographic factors to influence subsurface water dynamics, flowpaths, and water residence times (Beven and Kirkby, 1979; Wolock et al., 1990; Dillon and Molot, 1997; McGuire et al., 2005; Wagener et al., 2007), which altogether affects the accumulation of organic matter in flat, wet areas (Creed et al., 2003; Andersson & Nyberg, 2008; Creed et al., 2008). Steeper catchments tend to result in lower stream DOC concentrations (Eckhardt & Moore, 1990; Andersson & Nyberg, 2008; Li et al., 2015; Connolly et al., 2018; Musolff et al., 2018; Zarnetske et al., 2018; Jankowski & Schindler, 2019), as flat areas where flowpaths converge tend to accumulate organic matter more favourably (Andersson & Nyberg, 2009; Grabs et al., 2012; Ledesma et al., 2015; Musolff et al., 2018).

Organic soils, which in this area are generally located in depressional wetlands and riparian zones, are different from mineral soils in terms of their hydrology and biogeochemistry which changes the quantity and quality of organic matter in soil and the concentration and quality of DOM that ends up in streamwater (Berggren et al., 2007; Ågren et al., 2008a; Fellman et al., 2008; Kothawala et al., 2015). Organic soils have been shown to contribute most substantially to stream DOM quantity (Eckhardt and Moore, 1990; Creed et al., 2008; Laudon et al., 2004), particularly from riparian zones (Fiebig et al., 1990; Bishop et al., 1994; Grabs et al., 2012; Knorr, 2013; Ledesma et al., 2015; Musolff et al., 2018) and wetlands (Dillon & Molot, 1997; Hinton et al., 1998; Laudon et al., 2004; Ågren et al., 2007; Creed et al., 2008; Laudon et al., 2012; Walker et al., 2012; Winterdahl et al., 2014; Dick et al., 2015; Hytteborn et al., 2015; Monteith et al., 2015; Tiwari et al., 2017; Zarnetske et al., 2018; Casson et al., 2019). DOM from organic soils tends to be more aromatic and of a higher average molecular weight

(Kellerman et al., 2015; Wickland et al., 2007; Aukes et al., 2019). I found that organic soils contained soil leachate with higher DOM concentration and DOM which was more aromatic and of higher average molecular weight than mineral soils. Understanding how DOM varies across the landscape via soil leachate measurements coupled with measures of streamwater allows us to directly connect the DOM dynamics in streams to landscape sources.

5.2.1 Linking landscape sources of DOM to streamwater in 2021

Changes in DOM concentration and quality in streamwater over time and with changes in flow in 2021 can be linked to changing landscape sources of DOM (Broder et al., 2017; Birkel et al., 2017). Analyzing observations of DOM quality in stream in 2021, a drought year, allows us to test the hypothesis that stream DOM concentration and quality are related to landscape sources of DOM, in particular under the hydrological conditions discussed prior with the historical c-Q data. In 2021, I found that there were some similarities and some differences in DOM quality among streams, and also that DOM dynamics were often influenced by the onset and abatement of the drought.

During drought conditions, boreal streams receive DOM that has been processed more and is more aromatic (Broder et al., 2017; Tiwari et al., 2022), a result which was also found in all three streams despite catchment differences. In particular, DOM in streamwater was more aromatic and of higher average molecular weight during the drought compared with after the drought which occurred in 2021. Given that organic soils leach DOM which is more aromatic and of higher average molecular weight, I can say that during the drought it is most likely that streamwater DOM comes from organic soils. I may also infer that during the drought, DOM came from lower soil horizons where

DOM is altered due to biogeochemical processes and sorption (Inamdar et al., 2012; Kaiser & Kalbitz, 2012; Shen et al., 2015), however the bedrock depth in these Precambrian Shield catchments is quite shallow outside of near-stream organic soils which limits the soil depth variability of landscape DOM sources outside of these areas. Coupled with the knowledge that droughts lower water tables and reduce hydrological connectivity, these findings strongly indicate that deeper soil horizons and near-stream riparian zones and wetlands are the primary sources of streamwater DOM during the drought.

Hydrological events often mobilize fresh DOM to streams, particularly immediately following events (Pellerin et al., 2012; Wilson et al., 2013; Broder et al., 2017; Wagner et al., 2019), which explains the post-drought shift in both DOM quantity and quality in streamwater. Streamwater DOM load was highest and DOM quality was slightly less aromatic and of slightly lower average molecular weight following the post-drought flush, and this was found in both wetland-dominated and upland-dominated streams. The finding of DOM load being highest post-drought among all three streams shows both the hydrological disconnection between streams and landscape sources of DOM, as well as the warm, dry, aerated soil conditions which likely promoted production of DOM precursors which were later flushed to streams following the drought (Inamdar et al., 2008; Worrall et al., 2008; Raymond & Saiers, 2010; Mehring et al., 2013; Oswald & Branfireun, 2014; Tunalay et al., 2016; Werner et al., 2019; Fazekas et al., 2020; Blaurock et al., 2021, Tiwari et al., 2022). The observed shift in DOM quality among streams with different dominant landscape sources highlights the potential influence of droughts on stream DOM quality, particularly those with longer durations and greater severities (Blaurock et al., 2021; Wu et al., 2022). Combining the knowledge that DOM in streams post-drought is less aromatic and lower average molecular weight with the previous finding that DOM quality from mineral soils is less aromatic and of lower average molecular weight, I can say that post-drought DOM is coming proportionally more from mineral soils relative to during the drought. Coupled with increased hydrological connectivity, these findings indicate that DOM in streams post-drought has greater contributions from more surficial soil horizons and more distant sources as the catchment wets up.

In rewetting periods following droughts in boreal systems, changes in DOM quality are more pronounced in streams with lower proportions of wetlands (Tiwari et al., 2022). The stream draining the catchment with the highest proportion of wetlands had the smallest change in DOM aromaticity from drought to post-drought. The upland-dominated catchments had streams with substantial differences in DOM aromaticity following the post-drought flush, and particularly immediately following this event the difference in DOM was greatest. This suggests that DOM quality in wetland-dominated streams is more resilient to hydrological change, whereas upland-dominated catchments are more susceptible to sudden shifts in DOM quality as a result of hydrological change. Like DOM concentration (Schiff et al., 1998), DOM quality in wetland-dominated streams is more resilient to hydrological change because (a) water table and soil aeration conditions fluctuate less frequently (Broder et al., 2017), (b) wetlands buffer hydrological additions reaching streams (Lane et al., 2020), and (c) near-stream zones are typically the dominant stream source (Ducharme et al., 2021). Though I typically find source-switching more frequently in catchments with lower proportions of wetland, the drought conditions in this year caused the wetland-dominated stream to experience source-switching similar to mixed and forested catchments from other boreal landscapes (Berggren et al., 2008; Laudon et al., 2011).

The less aromatic, lower average molecular weight, and slightly less allochthonous DOM found in streamwater post-drought may also be a product of in-stream processing of DOM during drought-caused stagnation (Inamdar and Mitchell, 2007; Guarch-Ribot & Butturini 2016; Bernal et al., 2019; Granados et al., 2020), although changes of DOM quantity or quality in headwater streams are more likely the result of changes to landscape source (Singh et al., 2015; da Silva et al., 2021).

The range of DOM quality metrics indicate that DOM was always primarily of allochthonous origin. Lower values of FI (<= 1.3) and BIX (<= 0.7) indicate that there is almost no autochthonous production, and that DOM is primarily terrestrially-derived (McKnight et al., 2001; Huguet et al., 2009; Jaffé et al., 2012); in these streams the DOM had FI values < 1.25 and BIX < 0.6. Higher values of $SUVA_{254}$ point towards streamwater with DOM from organic landscape sources (Fleck et al., 2004; Olefeldt et al., 2013; Hansen et al., 2016), and lower values of $S_{275\text{-}295}$ point towards streamwater with DOM from terrestrial systems (Spencer et al., 2012). This means that in 2021 the DOM was always primarily terrestrially derived, a finding which is ubiquitous with headwater streams (Mulholland, 2003; Jonsson et al., 2007; Creed et al., 2015), due to their inherent interaction with terrestrial landscapes (Freeman et al., 2007).

5.2.2 Contextualizing the source and fate of DOM in 2021 within the historical data

Given that 2021 was a dry water year, I should expect the c-Q relationships to be similar to what was seen historically in dry water years. As the stream samples spanned from May 18 – Nov 2, it may be more helpful to compare the 2021 growing season stream samples to the historical post-snowmelt growing season (June 1- Nov 30). Given that the best predictors of DOC concentration in dry years during the post-snowmelt growing season were daily flow in the upland-large stream and 28-day AQ in the wetland-dominated and upland-small streams, these should be the most useful relationships to look at to compare 2021 to historical data. Based on the historical daily and antecedent c-Q analysis from dry water years post-snowmelt, I should expect to see a positive c-Q relationship in the upland-large stream (with daily flow) and negative c-Q relationships in the wetland-dominated and upland-small streams (with 28-day AQ) across the 2021 growing season. This was indeed what I saw in 2021. There appeared to be a threshold c-Q relationship in the upland-large stream, where DOM concentration only increased above a certain level of discharge, which is supported by previous research in Precambrian Shield watersheds, and at this study site showing that there is a threshold catchment storage capacity under which large parts of these catchments become hydrologically disconnected until these surface depressions effectively 'fill-and-spill' (Spence & Woo, 2003; Oswald et al., 2011). In the upland-small stream, I saw DOM concentration decrease with increasing 28-day AQ. And in the wetland-dominated stream, DOM concentration was lowest at times with high 28-day AQ. Overall, c-Q patterns in 2021 were clearly heavily influenced by the drought, with DOM concentration often distinct among time periods (pre-drought, drought, post-drought). This perhaps illustrates that although there are general trends in c-Q analyses across growing seasons, finer temporal resolution is required to better understand stream c-Q relationships (Strohmeier et al., 2013; Werner et al., 2019).

While c-Q relationships can help to infer DOM source, understanding how DOM quality changes with flow coupled with measurements of DOM quality at specific catchment locations is one way to confirm these c-Q based inferences. Given that the 2021 c-Q relationships during and after the drought were in-line with historical c-Q relationships, I can say that both the streamwater DOM quality and soil leachate DOM quality observed in 2021 can inform us not only about where the DOM comes from in this year, but also about where it is coming from in historical years. If I extrapolate 2021 to other dry years, I can say that in dry years, DOM comes from near-stream organic soils during lower flow, but from mineral soils when flow is higher. Given that c-Q relationships flip in the upland-dominated streams historically from dry to wet year, I can also estimate where the DOM is coming from in these wet years. In wet years, contributions of mineral soil DOM (in addition to the likely already present contributions of organic soils) to streams are proportionally greater at lower flow compared to dry years due to greater antecedent moisture and hydrological connectivity. Whereas at higher flow, both organic and mineral sources of DOM are likely diluted as diminishing returns in terms of hydrological connectivity are not enough to prevent source-limitation in stream c-Q relationships, even in wetland-dominated streams.

6. Conclusions

Boreal regions are experience disproportionately substantial climate change impacts (IPCC, 2014; Hansen et al., 2006; Kirtman et al., 2013; Abbott et al., 2016; Spinoni et al., 2018), and extreme hydrological conditions such as drought are predicted to occur with greater frequency and severity (IPCC, 2014; Hansen et al., 2012; Creed et al., 2015a; Büntgen et al., 2021), which has ramifications for the both the source and fate of DOM (Evans et al., 2005; Tranvik et al., 2009; Raymond & Saiers, 2010; Pagano et al., 2014; Prijac et al., 2023). Combined with previous research (Broder et al., 2017; Gómez-Gener et al., 2020; Wen et al., 2020; Gómez-Gener et al., 2021; Tiwari et al., 2022; Wardinski et al., 2022; Prijac et al., 2023), this study demonstrates how drought fundamentally affects DOM loading to downstream surface waters by influencing both the hydrology and biogeochemistry in headwater catchments. The onset and abatement of drought illustrated how severe hydrological disconnection can substantially affect the landscape source, quantity, and quality of DOM received in downstream surface waters. Under dry conditions, landscape sources of stream DOM are near-stream organic soils, while under wetter conditions the contributions of more distal mineral soils are more substantial. While concentration-discharge relationships both in this study and from other research show that DOM quantity and quality in headwater streams varies according to catchment proportions and spatial arrangements of landscape characteristics such as wetlands, and riparian zones, and upland areas (Williamson et al., 2008; Lintern et al., 2018; Brailsford et al., 2021), drought can cause streams to experience similar changes in DOM quantity and quality despite differences in catchment characteristics. This drought-induced DOM response has implications for headwater streams draining catchments with different landscape characteristics under climate change scenarios with more frequent and severe droughts. Pulses of DOM that is less aromatic and of lower molecular weight from these landscapes in post-drought flushes may influence downstream aquatic ecosystems and water quality (van Hees et al., 2005; Dittman et al., 2010; Aiken et al., 2011; Szkokan-Emilson et al., 2017; Kritzberg et al., 2020). Although drought can create similar situations among different catchments, the degree and timing of response in DOM concentration and quality differed among streams which illustrates the need to further understand local-scale landscape heterogeneity into account when making landscape-scale predictions about stream DOM dynamics (Schiff et al., 1998; Oswald et al., 2011; Laudon & Sponsellor, 2018; Creed et al., 2018; Yates et al., 2019; Fovet al., 2020; Wen et al., 2020; Gómez-Gener et al., 2021). While understanding how the source and fate of DOM is affected by climate change is complicated by the interacting control of climate drivers (e.g., changing precipitation, temperature) (Leach et al., 2016; Creed et al., 2018; Fork et al., 2020; Xenopoulos et al., 2021; Morison et al., 2022), the hydrological conditions and landscape characteristics of catchments have a clear influence on the DOM quantity and quality in receiving surface waters.

7. References

Abbott, B. W., Jones, J. B., Schuur, E. A. G., III, F. S. C., Bowden, W. B., Bret-Harte, M. S., Epstein, H. E., Flannigan, M. D., Harms, T. K., Hollingsworth, T. N., Mack, M. C., McGuire, A. D., Natali, S. M., Rocha, A. V., Tank, S. E., Turetsky, M. R., Vonk, J. E., Wickland, K. P., Aiken, G. R., … Zimov, S. (2016). Biomass offsets little or none of permafrost carbon release from soils, streams, and wildfire: An expert assessment. *Environmental Research Letters*, *11*(3), 034014. https://doi.org/10.1088/1748-9326/11/3/034014

Ågren, A., Buffam, I., Berggren, M., Bishop, K., Jansson, M., & Laudon, H. (2008a). Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer. *Journal of Geophysical Research: Biogeosciences*, *113*(G3). https://doi.org/10.1029/2007JG000674

Ågren, A., Jansson, M., Ivarsson, H., Bishop, K., & Seibert, J. (2008b). Seasonal and runoff-related changes in total organic carbon concentrations in the River Öre, Northern Sweden. *Aquatic Sciences*, *70*(1), 21–29. https://doi.org/10.1007/s00027-007-0943-9

Ågren, A., Buffam, I., Jansson, M., & Laudon, H. (2007). Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. *Journal of Geophysical Research: Biogeosciences*, *112*(G3). https://doi.org/10.1029/2006JG000381

Ågren, A., Buffam, I., Bishop, K., & Laudon, H. (2010). Modeling stream dissolved organic carbon concentrations during spring flood in the boreal forest: A simple empirical approach for regional predictions. *Journal of Geophysical Research: Biogeosciences*, *115*(G1). https://doi.org/10.1029/2009JG001013

Ågren, A. M., Buffam, I., Cooper, D. M., Tiwari, T., Evans, C. D., & Laudon, H. (2014). Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements? *Biogeosciences*, *11*(4), 1199–1213. https://doi.org/10.5194/bg-11-1199-2014

Aiken, G. R., Gilmour, C. C., Krabbenhoft, D. P., & Orem, W. (2011). Dissolved Organic Matter in the Florida Everglades: Implications for Ecosystem Restoration. *Critical Reviews in Environmental Science and Technology*, *41*(sup1), 217–248. https://doi.org/10.1080/10643389.2010.530934

Aitkenhead, J. A., Hope, D., & Billett, M. F. (1999). The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. *Hydrological Processes*, *13*(8), 1289–1302. https://doi.org/10.1002/(SICI)1099-1085(19990615)13:8<1289::AID-HYP766>3.0.CO;2-M

Akkanen, J., Tuikka, A., & Kukkonen, J. V. K. (2012). On the borderline of dissolved and particulate organic matter: Partitioning and bioavailability of polycyclic aromatic hydrocarbons. *Ecotoxicology and Environmental Safety*, *78*, 91–98. https://doi.org/10.1016/j.ecoenv.2011.11.010

Alexander, R. B., Boyer, E. W., Smith, R. A., Schwarz, G. E., & Moore, R. B. (2007). The Role of Headwater Streams in Downstream Water Quality. *JAWRA Journal of the American Water Resources Association*, *43*(1), 41–59. https://doi.org/10.1111/j.1752-1688.2007.00005.x

Andersson, J.-O., & Nyberg, L. (2008). Spatial variation of wetlands and flux of dissolved organic carbon in boreal headwater streams. *Hydrological Processes*, *22*(12), 1965–1975. https://doi.org/10.1002/hyp.6779

Andersson, J.-O., & Nyberg, L. (2009). Using official map data on topography, wetlands and vegetation cover for prediction of stream water chemistry in boreal headwater catchments. *Hydrology and Earth System Sciences*, *13*(4), 537–549. https://doi.org/10.5194/hess-13-537-2009

Aukes, P. J. K., Schiff, S. L., & Robertson, W. D. (2019). Evolution of Dissolved Organic Matter Along a Septic System Plume: Evidence of Sustained Biogeochemical Activity in the Groundwater Zone. *Journal of Geophysical Research: Biogeosciences*, *124*(6), 1389–1400. https://doi.org/10.1029/2018JG004758

Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., & Tranvik, L. J. (2009). The boundless carbon cycle. *Nature Geoscience*, *2*(9), 598–600. https://doi.org/10.1038/ngeo618

Bass, A. M., Bird, M. I., Liddell, M. J., & Nelson, P. N. (2011). Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment. *Limnology and Oceanography*, *56*(6), 2282–2292. https://doi.org/10.4319/lo.2011.56.6.2282

Bayley, S. E., Schindler, D. W., Beaty, K. G., Parker, B. R., & Stainton, M. P. (1992). Effects of Multiple Fires on Nutrient Yields from Streams Draining Boreal Forest and Fen Watersheds: Nitrogen and Phosphorus. *Canadian Journal of Fisheries and Aquatic Sciences*, *49*(3), 584–596. https://doi.org/10.1139/f92-068

Beaty, K. G., & Lyng, M. E. (1989). *Hydrometeorological data for the Experimental Lakes Area, northwestern Ontario, 1982 to 1987*. Department of Fisheries and Oceans, Central and Arctic Region.

Beven, K. J., & Kirkby, M. J. (1979). A physically based, variable contributing area model of basin hydrology / Un modèle à base physique de zone d'appel variable de l'hydrologie du bassin versant. *Hydrological Sciences Bulletin*, *24*(1), 43–69. https://doi.org/10.1080/02626667909491834

Birkel, C., Broder, T., & Biester, H. (2017). Nonlinear and threshold-dominated runoff generation controls DOC export in a small peat catchment. *Journal of Geophysical Research: Biogeosciences*, *122*(3), 498–513. https://doi.org/10.1002/2016JG003621

Bishop, K., Buffam, I., Erlandsson, M., Fölster, J., Laudon, H., Seibert, J., & Temnerud, J. (2008). Aqua Incognita: The unknown headwaters. *Hydrological Processes*, *22*(8), 1239–1242. https://doi.org/10.1002/hyp.7049

Bishop, K. H., Grip, H., & O'Neill, A. (1990). The origins of acid runoff in a hillslope during storm events. *Journal of Hydrology*, *116*(1), 35–61. https://doi.org/10.1016/0022-1694(90)90114-D

Bishop, K., Seibert, J., Nyberg, L., & Rodhe, A. (2011). Water storage in a till catchment. II: Implications of transmissivity feedback for flow paths and turnover times. *Hydrological Processes*, *25*(25), 3950–3959. https://doi.org/10.1002/hyp.8355

Bishop, K., Pettersson, C., Allard, B., & Lee, Y.-H. (1994). Identification of the riparian sources of aquatic dissolved organic carbon. *Environment International*, *20*(1), 11–19. https://doi.org/10.1016/0160-4120(94)90062-0

Bishop, K., Seibert, J., Köhler, S., & Laudon, H. (2004). Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrological Processes*, *18*(1), 185–189. https://doi.org/10.1002/hyp.5209

Blaurock, K., Beudert, B., Gilfedder, B. S., Fleckenstein, J. H., Peiffer, S., & Hopp, L. (2021). Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment. *Hydrology and Earth System Sciences*, *25*(9), 5133–5151. https://doi.org/10.5194/hess-25-5133-2021

Bolan, N. S., Adriano, D. C., Kunhikrishnan, A., James, T., McDowell, R., & Senesi, N. (2011). Dissolved Organic Matter. In *Advances in Agronomy* (Vol. 110, pp. 1–75). Elsevier. https://doi.org/10.1016/B978-0-12-385531-2.00001-3

Bottomley, D.J. 1974. Sources of streamflow and dissolved constituents in a small Precambrian Shield watershed. M.Sc. thesis, University of Waterloo, Waterloo, Ont.

Boyer, E. W., Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1997). Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes*, *11*(12), 1635–1647. https://doi.org/10.1002/(SICI)1099-1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H

Bradshaw, C. J. A., & Warkentin, I. G. (2015). Global estimates of boreal forest carbon stocks and flux. *Global and Planetary Change*, *128*, 24–30. https://doi.org/10.1016/j.gloplacha.2015.02.004

Brailsford, F. L., Glanville, H. C., Marshall, M. R., Yates, C. A., Owen, A. T., Golyshin, P. N., Johnes, P. J., & Jones, D. L. (2021). Land cover and nutrient enrichment regulates low-molecular weight dissolved organic matter turnover in freshwater ecosystems. *Limnology and Oceanography*, *66*(8), 2979–2987. https://doi.org/10.1002/lno.11852

Broder, T., Knorr, K.-H., & Biester, H. (2017). Changes in dissolved organic matter quality in a peatland and forest headwater stream as a function of seasonality and hydrologic conditions. *Hydrology and Earth System Sciences*, *21*(4), 2035–2051. https://doi.org/10.5194/hess-21-2035-2017

Brunskill, G. J., & Schindler, D. W. (1971). Geography and Bathymetry of Selected Lake Basins, Experimental Lakes Area, Northwestern Ontario. *Journal of the Fisheries Board of Canada*. https://doi.org/10.1139/f71-028

Buffam, I., Laudon, H., Temnerud, J., Mörth, C.-M., & Bishop, K. (2007). Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. *Journal of Geophysical Research: Biogeosciences*, *112*(G1). https://doi.org/10.1029/2006JG000218

Büntgen, U., Urban, O., Krusic, P. J., Rybníček, M., Kolář, T., Kyncl, T., Ač, A., Koňasová, E., Čáslavský, J., Esper, J., Wagner, S., Saurer, M., Tegel, W., Dobrovolný, P., Cherubini, P., Reinig, F., & Trnka, M. (2021). Recent European drought extremes beyond Common Era background variability. *Nature Geoscience*, *14*(4), Article 4. https://doi.org/10.1038/s41561-021-00698-0

Casson, N. J., Eimers, M. C., Watmough, S. A., & Richardson, M. C. (2019). The role of wetland coverage within the near-stream zone in predicting of seasonal stream export chemistry from forested headwater catchments. *Hydrological Processes*, *33*(10), 1465–1475. https://doi.org/10.1002/hyp.13413

Catalán, N., Marcé, R., Kothawala, D. N., & Tranvik, L. J. (2016). Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geoscience*, *9*(7), Article 7. https://doi.org/10.1038/ngeo2720

Chantigny, M. H. (2003). Dissolved and water-extractable organic matter in soils: A review on the influence of land use and management practices. *Geoderma*, *113*(3), 357–380. https://doi.org/10.1016/S0016-7061(02)00370-1

Chen, H., Zheng, B., Song, Y., & Qin, Y. (2011). Correlation between molecular absorption spectral slope ratios and fluorescence humification indices in characterizing CDOM. *Aquatic Sciences*, *73*(1), 103–112. https://doi.org/10.1007/s00027-010-0164-5

Chen, Y.-T., Wang, Y., & Yeh, K.-C. (2017). Role of root exudates in metal acquisition and tolerance. *Current Opinion in Plant Biology*, *39*, 66–72. https://doi.org/10.1016/j.pbi.2017.06.004

Clark, J. M., Bottrell, S. H., Evans, C. D., Monteith, D. T., Bartlett, R., Rose, R., Newton, R. J., & Chapman, P. J. (2010). The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of The Total Environment*, *408*(13), 2768–2775. https://doi.org/10.1016/j.scitotenv.2010.02.046

Clark, J. M., Lane, S. N., Chapman, P. J., & Adamson, J. K. (2008). Link between DOC in near surface peat and stream water in an upland catchment. *Science of The Total Environment*, *404*(2), 308–315. https://doi.org/10.1016/j.scitotenv.2007.11.002

Coble, P. G. (2007). Marine Optical Biogeochemistry: The Chemistry of Ocean Color. *Chemical Reviews*, *107*(2), 402–418. https://doi.org/10.1021/cr050350+

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., & Melack, J. (2007). Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems*, *10*(1), 172–185. https://doi.org/10.1007/s10021-006-9013-8

Connolly, C. T., Khosh, M. S., Burkart, G. A., Douglas, T. A., Holmes, R. M., Jacobson, A. D., Tank, S. E., & McClelland, J. W. (2018). Watershed slope as a predictor of fluvial dissolved organic matter and nitrate concentrations across geographical space and catchment size in the Arctic. *Environmental Research Letters*, *13*(10), 104015. https://doi.org/10.1088/1748-9326/aae35d

Cory, R. M., & McKnight, D. M. (2005). Fluorescence Spectroscopy Reveals Ubiquitous Presence of Oxidized and Reduced Quinones in Dissolved Organic Matter. *Environmental Science & Technology*, *39*(21), 8142–8149. https://doi.org/10.1021/es0506962

Covino, T. (2017). Hydrologic connectivity as a framework for understanding biogeochemical flux through watersheds and along fluvial networks. *Geomorphology*, *277*, 133–144. https://doi.org/10.1016/j.geomorph.2016.09.030

Creed, I. F., Beall, F. D., Clair, T. A., Dillon, P. J., & Hesslein, R. H. (2008). Predicting export of dissolved organic carbon from forested catchments in glaciated landscapes with shallow soils. *Global Biogeochemical Cycles*, *22*(4). https://doi.org/10.1029/2008GB003294

Creed, I. F., Bergström, A.-K., Trick, C. G., Grimm, N. B., Hessen, D. O., Karlsson, J., Kidd, K. A., Kritzberg, E., McKnight, D. M., Freeman, E. C., Senar, O. E., Andersson, A., Ask, J., Berggren, M., Cherif, M., Giesler, R., Hotchkiss, E. R., Kortelainen, P., Palta, M. M., … Weyhenmeyer, G. A. (2018). Global change-driven effects on dissolved organic matter composition: Implications for food webs of northern lakes. *Global Change Biology*, *24*(8), 3692–3714. https://doi.org/10.1111/gcb.14129

Creed, I. F., Hwang, T., Lutz, B., & Way, D. (2015a). Climate warming causes intensification of the hydrological cycle, resulting in changes to the vernal and autumnal windows in a northern temperate forest. *Hydrological Processes*, *29*(16), 3519–3534. https://doi.org/10.1002/hyp.10450

Creed IF, Band LE. 1998. Export of nitrogen from catchments within a temperate forest: Evidence for a unifying mechanism regulated by variable source area dynamics. Water Resources Research 34: 3105– 3120.

Creed, I. F., McKnight, D. M., Pellerin, B. A., Green, M. B., Bergamaschi, B. A., Aiken, G. R., Burns, D. A., Findlay, S. E. G., Shanley, J. B., Striegl, R. G., Aulenbach, B. T., Clow, D. W., Laudon, H., McGlynn, B. L., McGuire, K. J., Smith, R. A., & Stackpoole, S. M. (2015b). The river as a chemostat: Fresh perspectives on dissolved organic matter flowing down the river continuum. *Canadian Journal of Fisheries and Aquatic Sciences*, *72*(8), 1272–1285. https://doi.org/10.1139/cjfas-2014-0400

Creed, I. F., Sanford, S. E., Beall, F. D., Molot, L. A., & Dillon, P. J. (2003). Cryptic wetlands: Integrating hidden wetlands in regression models of the export of dissolved organic carbon from forested landscapes. *Hydrological Processes*, *17*(18), 3629–3648. https://doi.org/10.1002/hyp.1357 da Silva, M. P., Blaurock, K., Beudert, B., Fleckenstein, J. H., Hopp, L., Peiffer, S., Reemtsma, T., & Lechtenfeld, O. J. (2021). Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments. *Journal of Geophysical Research: Biogeosciences*, *126*(8), e2021JG006425. https://doi.org/10.1029/2021JG006425

D'Andrilli, J., Silverman, V., Buckley, S., & Rosario-Ortiz, F. L. (2022). Inferring Ecosystem Function from Dissolved Organic Matter Optical Properties: A Critical Review. *Environmental Science & Technology*, *56*(16), 11146–11161. https://doi.org/10.1021/acs.est.2c04240

D'Arcy, P., & Carignan, R. (1997). *Influence of catchment topography on water chemistry in southeastern Québec Shield lakes*. *54*.

Dawson, J. J. C., Malcolm, I. A., Middlemas, S. J., Tetzlaff, D., & Soulsby, C. (2009). Is the Composition of Dissolved Organic Carbon Changing in Upland Acidic Streams? *Environmental Science & Technology*, *43*(20), 7748–7753. https://doi.org/10.1021/es901649b

Dhillon, G. S., & Inamdar, S. (2014). Storm event patterns of particulate organic carbon (POC) for large storms and differences with dissolved organic carbon (DOC). *Biogeochemistry*, *118*(1), 61–81. https://doi.org/10.1007/s10533-013-9905-6

Dick, J. J., Tetzlaff, D., Birkel, C., & Soulsby, C. (2015). Modelling landscape controls on dissolved organic carbon sources and fluxes to streams. *Biogeochemistry*, *122*(2), 361–374. https://doi.org/10.1007/s10533-014-0046-3

Dillon, P. J., & Molot, L. A. (1997). Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. *Water Resources Research*, *33*(11), 2591–2600. https://doi.org/10.1029/97WR01921

Downing, J. A., Cole, J. J., Duarte, C. M., Middelburg, J. J., Melack, J. M., Prairie, Y. T., Kortelainen, P., Striegl, R. G., McDowell, W. H., & Tranvik, L. J. (2012). Global abundance and size distribution of streams and rivers. *Inland Waters*, *2*(4), 229–236. https://doi.org/10.5268/IW-2.4.502

Ducharme, A. A., Casson, N. J., Higgins, S. N., & Friesen-Hughes, K. (2021). Hydrological and catchment controls on event-scale dissolved organic carbon dynamics in boreal headwater streams. *Hydrological Processes*, *35*(7), e14279. https://doi.org/10.1002/hyp.14279

Eckhardt, B. W., & Moore, T. R. (1990). Controls on Dissolved Organic Carbon Concentrations in Streams, Southern Québec. *Canadian Journal of Fisheries and Aquatic Sciences*, *47*(8), 1537–1544. https://doi.org/10.1139/f90-173

Eimers, C., Buttle, J., & Watmough, S. (2008). Influence of seasonal changes in runoff and extreme events on dissolved organic carbon trends in wetland- and upland-draining streams. *Canadian Journal of Fisheries and Aquatic Sciences*, *65*, 796–808. https://doi.org/10.1139/f07-194

Elder, J. F., Rybicki, N. B., Carter, V., & Weintraub, V. (2000). Sources and yields of dissolved carbon in northern Wisconsin stream catchments with differing amounts of peatland. *Wetlands*, *20*(1), 113–125. https://doi.org/10.1672/0277-5212(2000)020[0113:SAYODC]2.0.CO;2

Emmerton, C. A., Beaty, K. G., Casson, N. J., Graydon, J. A., Hesslein, R. H., Higgins, S. N., Osman, H., Paterson, M. J., Park, A., & Tardif, J. C. (2019). Long-Term Responses of Nutrient Budgets to Concurrent Climate-Related Stressors in a Boreal Watershed. *Ecosystems*, *22*(2), 363–378. https://doi.org/10.1007/s10021-018-0276-7

Erlandsson, M., Cory, N., Fölster, J., Köhler, S., Laudon, H., Weyhenmeyer, G. A., & Bishop, K. (2011). Increasing Dissolved Organic Carbon Redefines the Extent of Surface Water Acidification and Helps Resolve a Classic Controversy. *BioScience*, *61*(8), 614–618. https://doi.org/10.1525/bio.2011.61.8.7

Evans, C. D., Monteith, D. T., & Cooper, D. M. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, *137*(1), 55–71. https://doi.org/10.1016/j.envpol.2004.12.031

Evans, C. D., Chapman, P. J., Clark, J. M., Monteith, D. T., & Cresser, M. S. (2006). Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology*, *12*(11), 2044–2053. https://doi.org/10.1111/j.1365-2486.2006.01241.x

Fazekas, H. M., Wymore, A. S., & McDowell, W. H. (2020). Dissolved Organic Carbon and Nitrate Concentration-Discharge Behavior Across Scales: Land Use, Excursions, and Misclassification. *Water Resources Research*, *56*(8), e2019WR027028. https://doi.org/10.1029/2019WR027028

Fellman, J. B., Hood, E., D'Amore, D. V., Edwards, R. T., & White, D. (2009). Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. *Biogeochemistry*, *95*(2), 277–293. https://doi.org/10.1007/s10533-009-9336-6

Fiebig, D. M., Lock, M. A., & Neal, C. (1990). Soil water in the riparian zone as a source of carbon for a headwater stream. *Journal of Hydrology*, *116*(1), 217–237. https://doi.org/10.1016/0022-1694(90)90124-G

Findlay, S., Quinn, J. M., Hickey, C. W., Burrell, G., & Downes, M. (2001). Effects of land use and riparian flowpath on delivery of dissolved organic carbon to streams. *Limnology and Oceanography*, *46*(2), 345–355. https://doi.org/10.4319/lo.2001.46.2.0345

Fisher, S. G., & Likens, G. E. (1972). Stream Ecosystem: Organic Energy Budget. *BioScience*, *22*(1), 33–35. https://doi.org/10.2307/1296183

Fleck, J. A., Bossio, D. A., & Fujii, R. (2004). Dissolved Organic Carbon and Disinfection By-Product Precursor Release from Managed Peat Soils. *Journal of Environmental Quality*, *33*(2), 465–475. https://doi.org/10.2134/jeq2004.4650

Fork, M. L., Sponseller, R. A., & Laudon, H. (2020). Changing Source-Transport Dynamics Drive Differential Browning Trends in a Boreal Stream Network. *Water Resources Research*, *56*(2), e2019WR026336. https://doi.org/10.1029/2019WR026336

Fovet, O., Cooper, D. M., Jones, D. L., Jones, T. G., & Evans, C. D. (2020). Dynamics of dissolved organic matter in headwaters: Comparison of headwater streams with contrasting DOM and nutrient composition. *Aquatic Sciences*, *82*(2), 29. https://doi.org/10.1007/s00027-020-0704-6

France, R., Steedman, R., Lehmann, R., & Peters, R. (2000). Landscape Modification of DOC Concentration in Boreal Lakes: Implications for UV-B Sensitivity. *Water, Air, and Soil Pollution*, *122*(1), 153–162. https://doi.org/10.1023/A:1005239721834

Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B., & Fenner, N. (2001). Export of organic carbon from peat soils. *Nature*, *412*(6849), Article 6849. https://doi.org/10.1038/35090628

Freeman, M. C., Pringle, C. M., & Jackson, C. R. (2007). Hydrologic Connectivity and the Contribution of Stream Headwaters to Ecological Integrity at Regional Scales. *JAWRA Journal of the American Water Resources Association*, *43*(1), 5–14. https://doi.org/10.1111/j.1752-1688.2007.00002.x

Gauthier, S., Bernier, P., Kuuluvainen, T., Shvidenko, A. Z., & Schepaschenko, D. G. (2015). Boreal forest health and global change. *Science*, *349*(6250), 819–822. https://doi.org/10.1126/science.aaa9092

Ged, E. C., & Boyer, T. H. (2013). Molecular weight distribution of phosphorus fraction of aquatic dissolved organic matter. *Chemosphere*, *91*(7), 921–927. https://doi.org/10.1016/j.chemosphere.2013.01.113

Gómez-Gener, L., Hotchkiss, E. R., Laudon, H., & Sponseller, R. A. (2021). Integrating Discharge-Concentration Dynamics Across Carbon Forms in a Boreal Landscape. *Water Resources Research*, *57*(8), e2020WR028806. https://doi.org/10.1029/2020WR028806

Gómez-Gener, L., Lupon, A., Laudon, H., & Sponseller, R. A. (2020). Drought alters the biogeochemistry of boreal stream networks. *Nature Communications*, *11*(1), Article 1. https://doi.org/10.1038/s41467-020-15496-2

Gomi, T., Sidle, R. C., & Richardson, J. S. (2002). Understanding Processes and Downstream Linkages of Headwater Systems: Headwaters differ from downstream reaches by their close coupling to hillslope processes, more temporal and spatial variation, and their need for different means of protection from land use. *BioScience*, *52*(10), 905–916. https://doi.org/10.1641/0006-3568(2002)052[0905:UPADLO]2.0.CO;2

Gorham, E. (1991). Northern Peatlands: Role in the Carbon Cycle and Probable Responses to Climatic Warming. *Ecological Applications*, *1*(2), 182–195. https://doi.org/10.2307/1941811

Gorham, E., Underwood, J. K., Janssens, J. A., Freedman, B., Maass, W., Waller, D. H., & Ogden, J. G. (1998). The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands. *Wetlands*, *18*(1), 115–132. https://doi.org/10.1007/BF03161449

Grabs, T., Bishop, K., Laudon, H., Lyon, S. W., & Seibert, J. (2012). Riparian zone hydrology and soil water total organic carbon (TOC): Implications for spatial variability and upscaling of lateral riparian TOC exports. *Biogeosciences*, *9*(10), 3901–3916. https://doi.org/10.5194/bg-9-3901-2012

Granados, V., Gutiérrez-Cánovas, C., Arias-Real, R., Obrador, B., Harjung, A., & Butturini, A. (2020). The interruption of longitudinal hydrological connectivity causes delayed responses in dissolved organic matter. *Science of The Total Environment*, *713*, 136619. https://doi.org/10.1016/j.scitotenv.2020.136619

Guarch-Ribot, A., & Butturini, A. (2016). Hydrological conditions regulate dissolved organic matter quality in an intermittent headwater stream. From drought to storm analysis. *Science of The Total Environment*, *571*, 1358–1369. https://doi.org/10.1016/j.scitotenv.2016.07.060

Guggenberger, G., & Zech, W. (1994). Dissolved organic carbon in forest floor leachates: Simple degradation products or humic substances? *Science of The Total Environment*, *152*(1), 37–47. https://doi.org/10.1016/0048-9697(94)90549-5

Haitzer, M., Höss, S., Traunspurger, W., & Steinberg, C. (1998). Effects of dissolved organic matter (DOM) on the bioconcentration of organic chemicals in aquatic organisms—A review—. *Chemosphere*, *37*(7), 1335–1362. https://doi.org/10.1016/S0045-6535(98)00117-9

Hale, R. L., & Godsey, S. E. (2019). Dynamic stream network intermittence explains emergent dissolved organic carbon chemostasis in headwaters. *Hydrological Processes*, *33*(13), 1926–1936. https://doi.org/10.1002/hyp.13455

Hall, B. D., Hesslein, R. H., Emmerton, C. A., Higgins, S. N., Ramlal, P., & Paterson, M. J. (2019). Multidecadal carbon sequestration in a headwater boreal lake. *Limnology and Oceanography*, *64*(S1), S150–S165. https://doi.org/10.1002/lno.11060

Hamond, H. F. (1990). Wetlands as the source of dissolved organic carbon to surface waters. *Organic acids in aquatic ecosystems*.

Hansen, J., Sato, M., & Ruedy, R. (2012). Perception of climate change. *Proceedings of the National Academy of Sciences*, *109*(37), E2415–E2423. https://doi.org/10.1073/pnas.1205276109

Hansen, J., Sato, M., Ruedy, R., Lo, K., Lea, D. W., & Medina-Elizade, M. (2006). Global temperature change. *Proceedings of the National Academy of Sciences*, *103*(39), 14288–14293. https://doi.org/10.1073/pnas.0606291103

Hansen, A. M., Kraus, T. E. C., Pellerin, B. A., Fleck, J. A., Downing, B. D., & Bergamaschi, B. A. (2016). Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation. *Limnology and Oceanography*, *61*(3), 1015–1032. https://doi.org/10.1002/lno.10270

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography*, *53*(3), 955–969. https://doi.org/10.4319/lo.2008.53.3.0955

Hinton, M. J., Schiff, S. L., & English, M. C. (1997). The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochemistry*, *36*(1), 67–88. https://doi.org/10.1023/A:1005779711821

Hinton, M. J., Schiff, S. L., & English, M. C. (1998). Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. *Biogeochemistry*, *41*(2), 175–197. https://doi.org/10.1023/A:1005903428956

Hood, E., Gooseff, M. N., & Johnson, S. L. (2006). Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. *Journal of Geophysical Research: Biogeosciences*, *111*(G1). https://doi.org/10.1029/2005JG000082

Hood, E., Williams, M. W., & McKnight, D. M. (2005). Sources of dissolved organic matter (DOM) in a Rocky Mountain stream using chemical fractionation and stable isotopes. *Biogeochemistry*, *74*(2), 231–255. https://doi.org/10.1007/s10533-004-4322-5

Hoogsteen, M. J. J., Lantinga, E. A., Bakker, E. J., Groot, J. C. J., & Tittonell, P. A. (2015). Estimating soil organic carbon through loss on ignition: Effects of ignition conditions and structural water loss. *European Journal of Soil Science*, *66*(2), 320–328. https://doi.org/10.1111/ejss.12224

Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1994). Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry*, *25*(3), 147–165. https://doi.org/10.1007/BF00024390

Horton RE. 1945. Erosional development of streams and their drainage basins—hydrophysical approach to quantitative morphology. Geol Soc Am Bull 56:275–370

Hoyt, A. M., Gandois, L., Eri, J., Kai, F. M., Harvey, C. F., & Cobb, A. R. (2019). CO2 emissions from an undrained tropical peatland: Interacting influences of temperature, shading and water table depth. *Global Change Biology*, *25*(9), 2885–2899. https://doi.org/10.1111/gcb.14702

Hugelius, G., Strauss, J., Zubrzycki, S., Harden, J. W., Schuur, E. a. G., Ping, C.-L., Schirrmeister, L., Grosse, G., Michaelson, G. J., Koven, C. D., O'Donnell, J. A., Elberling, B., Mishra, U., Camill, P., Yu, Z., Palmtag, J., & Kuhry, P. (2014). Estimated stocks of circumpolar permafrost carbon with quantified uncertainty ranges and identified data gaps. *Biogeosciences*, *11*(23), 6573–6593. https://doi.org/10.5194/bg-11-6573-2014

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., & Parlanti, E. (2009). Properties of fluorescent dissolved organic matter in the Gironde Estuary. *Organic Geochemistry*, *40*(6), 706–719. https://doi.org/10.1016/j.orggeochem.2009.03.002

Hur, J., & Kim, G. (2009). Comparison of the heterogeneity within bulk sediment humic substances from a stream and reservoir via selected operational descriptors. *Chemosphere*, *75*(4), 483–490. https://doi.org/10.1016/j.chemosphere.2008.12.056

Hytteborn, J. K., Temnerud, J., Alexander, R. B., Boyer, E. W., Futter, M. N., Fröberg, M., Dahné, J., & Bishop, K. H. (2015). Patterns and predictability in the intra-annual organic carbon variability across the boreal and hemiboreal landscape. *Science of The Total Environment*, *520*, 260–269. https://doi.org/10.1016/j.scitotenv.2015.03.041

Inamdar, S. P., Christopher, S. F., & Mitchell, M. J. (2004). Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrological Processes*, *18*(14), 2651–2661. https://doi.org/10.1002/hyp.5572

Inamdar, S., Rupp, J., & Mitchell, M. (2008). Differences in Dissolved Organic Carbon and Nitrogen Responses to Storm-Event and Ground-Water Conditions in a Forested, Glaciated Watershed in Western New York1. *JAWRA Journal of the American Water Resources Association*, *44*(6), 1458–1473. https://doi.org/10.1111/j.1752-1688.2008.00251.x

Inamdar, S., Finger, N., Singh, S., Mitchell, M., Levia, D., Bais, H., Scott, D., & McHale, P. (2012). Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA. *Biogeochemistry*, *108*(1), 55–76. https://doi.org/10.1007/s10533-011-9572-4

Inamdar, S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., Bais, H., & McHale, P. (2011). Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed. *Journal of Geophysical Research: Biogeosciences*, *116*(G3). https://doi.org/10.1029/2011JG001735

IPCC. Climate change 2014: impacts, adaptation, and vulnerability. Part A: global and sectoral aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (2014).

Jaffé, R., Yamashita, Y., Maie, N., Cooper, W. T., Dittmar, T., Dodds, W. K., Jones, J. B., Myoshi, T., Ortiz-Zayas, J. R., Podgorski, D. C., & Watanabe, A. (2012). Dissolved Organic Matter in Headwater Streams: Compositional Variability across Climatic Regions of North America. *Geochimica et Cosmochimica Acta*, *94*, 95–108. https://doi.org/10.1016/j.gca.2012.06.031

Jaffé, R., McKnight, D., Maie, N., Cory, R., McDowell, W. H., & Campbell, J. L. (2008). Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. *Journal of Geophysical Research: Biogeosciences*, *113*(G4). https://doi.org/10.1029/2008JG000683

Jager, D. F., Wilmking, M., & Kukkonen, J. V. K. (2009). The influence of summer seasonal extremes on dissolved organic carbon export from a boreal peatland catchment: Evidence from one dry and one wet growing season. *Science of The*

Total Environment, *407*(4), 1373–1382.
https://doi.org/10.1016/j.scitotenv.2008.10.005

Jankowski, K. J., & Schindler, D. E. (2019). Watershed geomorphology modifies the sensitivity of aquatic ecosystem metabolism to temperature. *Scientific Reports*, *9*(1), Article 1. https://doi.org/10.1038/s41598-019-53703-3

Jansson, M., Persson, L., De Roos, A. M., Jones, R. I., & Tranvik, L. J. (2007). Terrestrial carbon and intraspecific size-variation shape lake ecosystems. *Trends in Ecology & Evolution*, *22*(6), 316–322. https://doi.org/10.1016/j.tree.2007.02.015

Johnson, L., Richards, C., Host, G., & Arthur, J. (1997). Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshwater Biology*, *37*(1), 193–208. https://doi.org/10.1046/j.1365-2427.1997.d01-539.x

Jonsson, A., Algesten, G., Bergström, A.-K., Bishop, K., Sobek, S., Tranvik, L. J., & Jansson, M. (2007). Integrating aquatic carbon fluxes in a boreal catchment carbon budget. *Journal of Hydrology*, *334*(1), 141–150. https://doi.org/10.1016/j.jhydrol.2006.10.003

Kaiser, K., & Kalbitz, K. (2012). Cycling downwards – dissolved organic matter in soils. *Soil Biology and Biochemistry*, *52*, 29–32. https://doi.org/10.1016/j.soilbio.2012.04.002

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., & Matzner, E. (2000). CONTROLS ON THE DYNAMICS OF DISSOLVED ORGANIC MATTER IN SOILS: A REVIEW. *Soil Science*, *165*(4), 277–304.

Kane, E. S., Mazzoleni, L. R., Kratz, C. J., Hribljan, J. A., Johnson, C. P., Pypker, T. G., & Chimner, R. (2014). Peat porewater dissolved organic carbon concentration and lability increase with warming: A field temperature manipulation experiment in a poor-fen. *Biogeochemistry*, *119*(1), 161–178. https://doi.org/10.1007/s10533-014-9955-4

Kane, E. S., Valentine, D. W., Michaelson, G. J., Fox, J. D., & Ping, C.-L. (2006). Controls over pathways of carbon efflux from soils along climate and black spruce productivity gradients in interior Alaska. *Soil Biology and Biochemistry*, *38*(6), 1438–1450. https://doi.org/10.1016/j.soilbio.2005.11.004

Kaplan, L. A., & Cory, R. M. (2016). Chapter 6 - Dissolved Organic Matter in Stream Ecosystems: Forms, Functions, and Fluxes of Watershed Tea. In J. B. Jones & E. H. Stanley (Eds.), *Stream Ecosystems in a Changing Environment* (pp. 241–320). Academic Press. https://doi.org/10.1016/B978-0-12-405890-3.00006-3

Karlsson, J., Berggren, M., Ask, J., Byström, P., Jonsson, A., Laudon, H., & Jansson, M. (2012). Terrestrial organic matter support of lake food webs: Evidence from lake metabolism and stable hydrogen isotopes of consumers. *Limnology and Oceanography*, *57*(4), 1042–1048. https://doi.org/10.4319/lo.2012.57.4.1042

Kayranli, B., Scholz, M., Mustafa, A., & Hedmark, Å. (2010). Carbon Storage and Fluxes within Freshwater Wetlands: A Critical Review. *Wetlands*, *30*(1), 111–124. https://doi.org/10.1007/s13157-009-0003-4

Kellerman, A. M., Kothawala, D. N., Dittmar, T., & Tranvik, L. J. (2015). Persistence of dissolved organic matter in lakes related to its molecular characteristics. *Nature Geoscience*, *8*(6), Article 6. https://doi.org/10.1038/ngeo2440

Kirtman, B., S.B. Power, J.A. Adedoyin, G.J. Boer, R. Bojariu, I. Camilloni, F.J. Doblas-Reyes, A.M. Fiore, M. Kimoto, G.A. Meehl, M. Prather, A. Sarr, C. Schär, R.

Sutton, G.J. van Oldenborgh, G. Vecchi and H.J. Wang, 2013: Near-term Climate Change: Projections and Predictability. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Knorr, K.-H. (2013). DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths – are DOC exports mediated by iron reduction/oxidation cycles? *Biogeosciences*, *10*(2), 891–904. https://doi.org/10.5194/bg-10-891-2013

Köhler, S. J., Buffam, I., Laudon, H., & Bishop, K. H. (2008). Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. *Journal of Geophysical Research: Biogeosciences*, *113*(G3). https://doi.org/10.1029/2007JG000629

Köhler, S. J., Buffam, I., Seibert, J., Bishop, K. H., & Laudon, H. (2009). Dynamics of stream water TOC concentrations in a boreal headwater catchment: Controlling factors and implications for climate scenarios. *Journal of Hydrology*, *373*(1–2), 44–56. https://doi.org/10.1016/j.jhydrol.2009.04.012

Kothawala, D. N., Ji, X., Laudon, H., Ågren, A. M., Futter, M. N., Köhler, S. J., & Tranvik, L. J. (2015). The relative influence of land cover, hydrology, and in-stream processing on the composition of dissolved organic matter in boreal streams.

Journal of Geophysical Research: Biogeosciences, *120*(8), 1491–1505. https://doi.org/10.1002/2015JG002946

Kritzberg, E. S., Hasselquist, E. M., Škerlep, M., Löfgren, S., Olsson, O., Stadmark, J., Valinia, S., Hansson, L.-A., & Laudon, H. (2020). Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. *Ambio*, *49*(2), 375–390. https://doi.org/10.1007/s13280-019-01227-5

LaCroix, R. E., Tfaily, M. M., McCreight, M., Jones, M. E., Spokas, L., & Keiluweit, M. (2019). Shifting mineral and redox controls on carbon cycling in seasonally flooded mineral soils. *Biogeosciences*, *16*(13), 2573–2589. https://doi.org/10.5194/bg-16-2573-2019

Lane, D., McCarter, C. P. R., Richardson, M., McConnell, C., Field, T., Yao, H., Arhonditsis, G., & Mitchell, C. P. J. (2020). Wetlands and low-gradient topography are associated with longer hydrologic transit times in Precambrian Shield headwater catchments. *Hydrological Processes*, *34*(3), 598–614. https://doi.org/10.1002/hyp.13609

Laudon, H., & Buffam, I. (2008). Impact of changing DOC concentrations on the potential distribution of acid sensitive biota in a boreal stream network. *Hydrol. Earth Syst. Sci.*

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., & Köhler, S. (2011). Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling. *Ecosystems*, *14*(6), 880–893. https://doi.org/10.1007/s10021-011-9452-8

Laudon, H., Buttle, J., Carey, S. K., McDonnell, J., McGuire, K., Seibert, J., Shanley, J., Soulsby, C., & Tetzlaff, D. (2012). Cross-regional prediction of long-term trajectory of stream water DOC response to climate change. *Geophysical Research Letters*, *39*(18). https://doi.org/10.1029/2012GL053033

Laudon, H., Köhler, S., & Buffam, I. (2004). Seasonal TOC export from seven boreal catchments in northern Sweden. *Aquatic Sciences*, *66*(2), 223–230. https://doi.org/10.1007/s00027-004-0700-2

Laudon, H., & Slaymaker, O. (1997). Hydrograph separation using stable isotopes, silica and electrical conductivity: An alpine example. *Journal of Hydrology*, *201*(1), 82–101. https://doi.org/10.1016/S0022-1694(97)00030-9

Laudon, H., & Sponseller, R. A. (2018). How landscape organization and scale shape catchment hydrology and biogeochemistry: Insights from a long-term catchment study. *WIREs Water*, *5*(2), e1265. https://doi.org/10.1002/wat2.1265

Laudon, H., Tetzlaff, D., Soulsby, C., Carey, S., Seibert, J., Buttle, J., Shanley, J., McDonnell, J. J., & McGuire, K. (2013). Change in winter climate will affect dissolved organic carbon and water fluxes in mid-to-high latitude catchments. *Hydrological Processes*, *27*(5), 700–709. https://doi.org/10.1002/hyp.9686

Lavonen, E. E., Gonsior, M., Tranvik, L. J., Schmitt-Kopplin, P., & Köhler, S. J. (2013). Selective Chlorination of Natural Organic Matter: Identification of Previously Unknown Disinfection Byproducts. *Environmental Science & Technology*, *47*(5), 2264–2271. https://doi.org/10.1021/es304669p

Lawlor, A. J., & Tipping, E. (2003). Metals in bulk deposition and surface waters at two upland locations in northern England. *Environmental Pollution*, *121*(2), 153–167. https://doi.org/10.1016/S0269-7491(02)00228-2

Leach, J. A., Larsson, A., Wallin, M. B., Nilsson, M. B., & Laudon, H. (2016). Twelve year interannual and seasonal variability of stream carbon export from a boreal peatland catchment. *Journal of Geophysical Research: Biogeosciences*, *121*(7), 1851–1866. https://doi.org/10.1002/2016JG003357

Ledesma, J. L. J., Grabs, T., Bishop, K. H., Schiff, S. L., & Köhler, S. J. (2015). Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. *Global Change Biology*, *21*(8), 2963–2979. https://doi.org/10.1111/gcb.12872

Ledesma, J. L. J., Köhler, S. J., & Futter, M. N. (2012). Long-term dynamics of dissolved organic carbon: Implications for drinking water supply. *Science of The Total Environment*, *432*, 1–11. https://doi.org/10.1016/j.scitotenv.2012.05.071

Ledesma, J. L. J., Kothawala, D. N., Bastviken, P., Maehder, S., Grabs, T., & Futter, M. N. (2018a). Stream Dissolved Organic Matter Composition Reflects the Riparian Zone, Not Upslope Soils in Boreal Forest Headwaters. *Water Resources Research*, *54*(6), 3896–3912. https://doi.org/10.1029/2017WR021793

Ledesma, J. L. J., Futter, M. N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R. A., Laudon, H., Bishop, K. H., & Köhler, S. J. (2018b). Towards an Improved Conceptualization of Riparian Zones in Boreal Forest Headwaters. *Ecosystems*, *21*(2), 297–315. https://doi.org/10.1007/s10021-017-0149-5

Li, M., del Giorgio, P. A., Parkes, A. H., & Prairie, Y. T. (2015). The relative influence of topography and land cover on inorganic and organic carbon exports from catchments in southern Quebec, Canada. *Journal of Geophysical Research: Biogeosciences*, *120*(12), 2562–2578. https://doi.org/10.1002/2015JG003073

Limpens, J., Berendse, F., Blodau, C., Canadell, J. G., Freeman, C., Holden, J., Roulet, N., Rydin, H., & Schaepman-Strub, G. (2008). Peatlands and the carbon cycle: From local processes to global implications – a synthesis. *Biogeosciences*, *5*(5), 1475–1491. https://doi.org/10.5194/bg-5-1475-2008

Lintern, A., Webb, J. a., Ryu, D., Liu, S., Bende-Michl, U., Waters, D., Leahy, P., Wilson, P., & Western, A. W. (2018). Key factors influencing differences in stream water quality across space. *WIREs Water*, *5*(1), e1260. https://doi.org/10.1002/wat2.1260

Lowe, W. H., & Likens, G. E. (2005). Moving Headwater Streams to the Head of the Class. *BioScience*, *55*(3), 196–197. https://doi.org/10.1641/0006-3568(2005)055[0196:MHSTTH]2.0.CO;2

Luke, S. H., Luckai, N. J., Burke, J. M., & Prepas, E. E. (2007). Riparian areas in the Canadian boreal forest and linkages with water quality in streams. *Environmental Reviews*, *15*(NA), 79–97. https://doi.org/10.1139/A07-001

Manzoni, S., & Porporato, A. (2011). Common hydrologic and biogeochemical controls along the soil–stream continuum. *Hydrological Processes*, *25*(8), 1355–1360. https://doi.org/10.1002/hyp.7938

Maranger, R., & Pullin, M. J. (2003). 8 - Elemental Complexation by Dissolved Organic Matter in Lakes: Implications for Fe Speciation and the Speciation and the

Bioavailability of Fe and P. In S. E. G. Findlay & R. L. Sinsabaugh (Eds.), *Aquatic Ecosystems* (pp. 185–214). Academic Press. https://doi.org/10.1016/B978-012256371-3/50009-3

Mattsson, T., Kortelainen, P., & Räike, A. (2005). Export of DOM from Boreal Catchments: Impacts of Land Use Cover and Climate. *Biogeochemistry*, *76*(2), 373–394. https://doi.org/10.1007/s10533-005-6897-x

McDowell, W. H. (2003). Dissolved organic matter in soils—Future directions and unanswered questions. *Geoderma*, *113*(3), 179–186. https://doi.org/10.1016/S0016-7061(02)00360-9

McDowell, W. H., & Likens, G. E. (1988). Origin, Composition, and Flux of Dissolved Organic Carbon in the Hubbard Brook Valley. *Ecological Monographs*, *58*(3), 177–195. https://doi.org/10.2307/2937024

McDowell WH, Fisher SG (1976) Autumnal processing of dissolved organic matter in a small woodland stream ecosystem. Ecology 57:561–569

McGuire, K. J., & McDonnell, J. J. (2010). Hydrological connectivity of hillslopes and streams: Characteristic time scales and nonlinearities. *Water Resources Research*, *46*(10). https://doi.org/10.1029/2010WR009341

McGuire, K. J., McDonnell, J. J., Weiler, M., Kendall, C., McGlynn, B. L., Welker, J. M., & Seibert, J. (2005). The role of topography on catchment-scale water residence time. *Water Resources Research*, *41*(5). https://doi.org/10.1029/2004WR003657

Mehring, A. S., Lowrance, R. R., Helton, A. M., Pringle, C. M., Thompson, A., Bosch, D. D., & Vellidis, G. (2013). Interannual drought length governs dissolved organic carbon dynamics in blackwater rivers of the western upper Suwannee River basin:

DROUGHT AND DOC IN BLACKWATER RIVERS. *Journal of Geophysical Research: Biogeosciences*, *118*(4), 1636–1645. https://doi.org/10.1002/2013JG002415

Meyer, J. L., & Wallace, J. B. (2001). Lost linkages and lotic ecology: Rediscovering small streams. *Ecology: Achievement and Challenge: The 41st Symposium of the British Ecological Society Sponsored by the Ecological Society of America Held at Orlando, Florida, USA, 10-13 April 2000*, 295–317.

Mierle, G., & Ingram, R. (1991). The role of humic substances in the mobilization of mercury from watersheds. *Water Air & Soil Pollution*, *56*(1), 349–357. https://doi.org/10.1007/BF00342282

Moatar, F., Abbott, B. W., Minaudo, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, *53*(2), 1270–1287. https://doi.org/10.1002/2016WR019635

Moore, T. R., & Dalva, M. (1993). The influence of temperature and water table position on carbon dioxide and methane emissions from laboratory columns of peatland soils. *Journal of Soil Science*, *44*(4), 651–664. https://doi.org/10.1111/j.1365-2389.1993.tb02330.x

Morison, M. Q., Higgins, S. N., Webster, K. L., Emilson, E. J. S., Yao, H., & Casson, N. J. (2022). Spring coherence in dissolved organic carbon export dominates total coherence in Boreal Shield forested catchments. *Environmental Research Letters*, *17*(1), 014048. https://doi.org/10.1088/1748-9326/ac462f

Mosher, J. J., Kaplan, L. A., Podgorski, D. C., McKenna, A. M., & Marshall, A. G. (2015). Longitudinal shifts in dissolved organic matter chemogeography and chemodiversity within headwater streams: A river continuum reprise. *Biogeochemistry*, *124*(1), 371–385. https://doi.org/10.1007/s10533-015-0103-6

Mueller, B., den Haan, J., Visser, P. M., Vermeij, M. J. A., & van Duyl, F. C. (2016). Effect of light and nutrient availability on the release of dissolved organic carbon (DOC) by Caribbean turf algae. *Scientific Reports*, *6*(1), 23248. https://doi.org/10.1038/srep23248

Mulholland, P. J. (2003). 6—Large-Scale Patterns in Dissolved Organic Carbon Concentration, Flux, and Sources. In S. E. G. Findlay & R. L. Sinsabaugh (Eds.), *Aquatic Ecosystems* (pp. 139–159). Academic Press. https://doi.org/10.1016/B978-012256371-3/50007-X

Musolff, A., Fleckenstein, J. H., Opitz, M., Büttner, O., Kumar, R., & Tittel, J. (2018). Spatio-temporal controls of dissolved organic carbon stream water concentrations. *Journal of Hydrology*, *566*, 205–215. https://doi.org/10.1016/j.jhydrol.2018.09.011

Nadeau, T.-L., & Rains, M. C. (2007). Hydrological Connectivity Between Headwater Streams and Downstream Waters: How Science Can Inform Policy1. *JAWRA Journal of the American Water Resources Association*, *43*(1), 118–133. https://doi.org/10.1111/j.1752-1688.2007.00010.x

Nyberg, L., Stähli, M., Mellander, P.-E., & Bishop, K. H. (2001). Soil frost effects on soil water and runoff dynamics along a boreal forest transect: 1. Field investigations. *Hydrological Processes*, *15*(6), 909–926. https://doi.org/10.1002/hyp.256

O'Donnell, J. A., Harden, J. W., McGuire, A. D., Kanevskiy, M. Z., Jorgenson, M. T., & Xu, X. (2011). The effect of fire and permafrost interactions on soil carbon accumulation in an upland black spruce ecosystem of interior Alaska: Implications for post-thaw carbon loss. *Global Change Biology*, *17*(3), 1461–1474. https://doi.org/10.1111/j.1365-2486.2010.02358.x

Olefeldt, D., Turetsky, M. R., & Blodau, C. (2013). Altered Composition and Microbial versus UV-Mediated Degradation of Dissolved Organic Matter in Boreal Soils Following Wildfire. *Ecosystems*, *16*(8), 1396–1412. https://doi.org/10.1007/s10021-013-9691-y

Oswald, C. J., Richardson, M. C., & Branfireun, B. A. (2011). Water storage dynamics and runoff response of a boreal Shield headwater catchment. *Hydrological Processes*, *25*(19), 3042–3060. https://doi.org/10.1002/hyp.8036

Oswald, C. J., & Branfireun, B. A. (2014). Antecedent moisture conditions control mercury and dissolved organic carbon concentration dynamics in a boreal headwater catchment. *Water Resources Research*, *50*(8), 6610–6627. https://doi.org/10.1002/2013WR014736

Pacific, V. J., Jencso, K. G., & McGlynn, B. L. (2010). Variable flushing mechanisms and landscape structure control stream DOC export during snowmelt in a set of nested catchments. *Biogeochemistry*, *99*(1), 193–211. https://doi.org/10.1007/s10533-009-9401-1

Pagano, T., Bida, M., & Kenny, J. E. (2014). Trends in Levels of Allochthonous Dissolved Organic Carbon in Natural Water: A Review of Potential Mechanisms under a Changing Climate. *Water*, *6*(10), Article 10. https://doi.org/10.3390/w6102862

Pan, Y., Birdsey, R. A., Fang, J., Houghton, R., Kauppi, P. E., Kurz, W. A., Phillips, O. L., Shvidenko, A., Lewis, S. L., Canadell, J. G., Ciais, P., Jackson, R. B., Pacala, S. W., McGuire, A. D., Piao, S., Rautiainen, A., Sitch, S., & Hayes, D. (2011). A Large and Persistent Carbon Sink in the World's Forests. *Science*, *333*(6045), 988–993. https://doi.org/10.1126/science.1201609

Parker, B. R. P. R., Schindler, D. W. S. W., Beaty, K. G. B. G., Stainton, M. P. S. P., & Kasian, S. E. M. K. E. M. (2009). Long-term changes in climate, streamflow, and nutrient budgets for first-order catchments at the Experimental Lakes Area (Ontario, Canada)This paper is part of the series "Forty Years of Aquatic Research at the Experimental Lakes Area". *Canadian Journal of Fisheries and Aquatic Sciences*. https://doi.org/10.1139/F09-149

Pattanaik, B., Wulff, A., Roleda, M. Y., Garde, K., & Mohlin, M. (2010). Production of the cyanotoxin nodularin—A multifactorial approach. *Harmful Algae*, *10*(1), 30–38. https://doi.org/10.1016/j.hal.2010.06.001

Penna, D., van Meerveld, H. J., Oliviero, O., Zuecco, G., Assendelft, R. S., Dalla Fontana, G., & Borga, M. (2015). Seasonal changes in runoff generation in a small forested mountain catchment. *Hydrological Processes*, *29*(8), 2027–2042. https://doi.org/10.1002/hyp.10347

Peralta-Tapia, A., Sponseller, R. A., Tetzlaff, D., Soulsby, C., & Laudon, H. (2015). Connecting precipitation inputs and soil flow pathways to stream water in contrasting boreal catchments. *Hydrological Processes*, *29*(16), 3546–3555. https://doi.org/10.1002/hyp.10300

Pisani, O., Bosch, D. D., Coffin, A. W., Endale, D. M., Liebert, D., & Strickland, T. C. (2020). Riparian land cover and hydrology influence stream dissolved organic matter composition in an agricultural watershed. *Science of The Total Environment*, *717*, 137165. https://doi.org/10.1016/j.scitotenv.2020.137165

Ploum, S. W., Laudon, H., Peralta-Tapia, A., & Kuglerová, L. (2020). Are dissolved organic carbon concentrations in riparian groundwater linked to hydrological pathways in the boreal forest? *Hydrology and Earth System Sciences*, *24*(4), 1709–1720. https://doi.org/10.5194/hess-24-1709-2020

Price, J. S., & Waddington, J. M. (2000). Advances in Canadian wetland hydrology an biogeochemistry. *Hydrological Processes*, *14*(9), 1579–1589. https://doi.org/10.1002/1099-1085(20000630)14:9<1579::AID-HYP76>3.0.CO;2-#

Price, D. T., Alfaro, R. I., Brown, K. J., Flannigan, M. D., Fleming, R. A., Hogg, E. H., Girardin, M. P., Lakusta, T., Johnston, M., McKenney, D. W., Pedlar, J. H., Stratton, T., Sturrock, R. N., Thompson, I. D., Trofymow, J. A., & Venier, L. A. (2013). Anticipating the consequences of climate change for Canada's boreal forest ecosystems. *Environmental Reviews*, *21*(4), 322–365. https://doi.org/10.1139/er-2013-0042

Prijac, A., Gandois, L., Taillardat, P., Bourgault, M.-A., Riahi, K., Ponçot, A., Tremblay, A., & Garneau, M. (2023). *Hydrological connectivity controls dissolved organic carbon exports in a peatland-dominated boreal catchment stream* [Preprint].

Biogeochemical processes/Instruments and observation techniques. https://doi.org/10.5194/hess-2022-426

Pucher, M., Wünsch, U., Weigelhofer, G., Murphy, K., Hein, T., & Graeber, D. (2019). staRdom: Versatile Software for Analyzing Spectroscopic Data of Dissolved Organic Matter in R. *Water*, *11*(11), Article 11. https://doi.org/10.3390/w11112366

Qualls, R. G., & Richardson, C. J. (2003). Factors controlling concentration, export, and decomposition of dissolved organic nutrients in the Everglades of Florida. *Biogeochemistry*, *62*(2), 197–229. https://doi.org/10.1023/A:1021150503664

Rasilo, T., Ojala, A., Huotari, J., Starr, M., & Pumpanen, J. (2015). Concentrations and quality of DOC along the terrestrial–aquatic continuum in a boreal forested catchment. *Freshwater Science*, *34*(2), 440–455. https://doi.org/10.1086/680682

Ravichandran, M. (2004). Interactions between mercury and dissolved organic matter––a review. *Chemosphere*, *55*(3), 319–331. https://doi.org/10.1016/j.chemosphere.2003.11.011

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., & Guth, P. (2013). Global carbon dioxide emissions from inland waters. *Nature*, *503*(7476), Article 7476. https://doi.org/10.1038/nature12760

Raymond, P. A., & Saiers, J. E. (2010). Event controlled DOC export from forested watersheds. *Biogeochemistry*, *100*(1), 197–209. https://doi.org/10.1007/s10533-010-9416-7

Raymond, P. A., Saiers, J. E., & Sobczak, W. V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. *Ecology*, *97*(1), 5–16. https://doi.org/10.1890/14-1684.1

Ritson, J. P., Bell, M., Graham, N. J. D., Templeton, M. R., Brazier, R. E., Verhoef, A., Freeman, C., & Clark, J. M. (2014). Simulated climate change impact on summer dissolved organic carbon release from peat and surface vegetation: Implications for drinking water treatment. *Water Research*, *67*, 66–76. https://doi.org/10.1016/j.watres.2014.09.015

Rodríguez-Cardona, B. M., Wymore, A. S., Argerich, A., Barnes, R. T., Bernal, S., Brookshire, E. N. J., Coble, A. A., Dodds, W. K., Fazekas, H. M., Helton, A. M., Johnes, P. J., Johnson, S. L., Jones, J. B., Kaushal, S. S., Kortelainen, P., López-Lloreda, C., Spencer, R. G. M., & McDowell, W. H. (2022). Shifting stoichiometry: Long-term trends in stream-dissolved organic matter reveal altered C:N ratios due to history of atmospheric acid deposition. *Global Change Biology*, *28*(1), 98–114. https://doi.org/10.1111/gcb.15965

Roulet, N. T., Lafleur, P. M., Richard, P. J. H., Moore, T. R., Humphreys, E. R., & Bubier, J. (2007). Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland. *Global Change Biology*, *13*(2), 397–411. https://doi.org/10.1111/j.1365-2486.2006.01292.x

Ruess, R. W., Hendrick, R. L., Burton, A. J., Pregitzer, K. S., Sveinbjornssön, B., Allen, M. F., & Maurer, G. E. (2003). Coupling Fine Root Dynamics with Ecosystem Carbon Cycling in Black Spruce Forests of Interior Alaska. *Ecological Monographs*, *73*(4), 643–662. https://doi.org/10.1890/02-4032

Sanderman, J., Lohse, K. A., Baldock, J. A., & Amundson, R. (2009). Linking soils and streams: Sources and chemistry of dissolved organic matter in a small coastal watershed. *Water Resources Research*, *45*(3). https://doi.org/10.1029/2008WR006977

Schiff, S., Aravena, R., Mewhinney, E., Elgood, R., Warner, B., Dillon, P., & Trumbore, S. (1998). Precambrian Shield Wetlands: Hydrologic Control of the Sources and Export of Dissolved Organic Matter. *Climatic Change*, *40*(2), 167–188. https://doi.org/10.1023/A:1005496331593

Schindler, D. W., Bayley, S. E., Parker, B. R., Beaty, K. G., Cruikshank, D. R., Fee, E. J., Schindler, E. U., & Stainton, M. P. (1996). The effects of climatic warming on the properties of boreal lakes and streams at the Experimental Lakes Area, northwestern Ontario. *Limnology and Oceanography*, *41*(5), 1004–1017. https://doi.org/10.4319/lo.1996.41.5.1004

Schindler, D. W., Curtis, P. J., Bayley, S. E., Parker, B. R., Beaty, K. G., & Stainton, M. P. (1997). Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. *Biogeochemistry*, *36*(1), 9–28. https://doi.org/10.1023/A:1005792014547

Sebestyen, S. D., Funke, M., & Cotner, J. B. (2021). Sources and biodegradability of dissolved organic matter in two headwater peatland catchments at the Marcell Experimental Forest, northern Minnesota, USA. *Hydrological Processes*, *n/a*(n/a), e14049. https://doi.org/10.1002/hyp.14049

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., & Bishop, K. (2009). Linking soil- and stream-water chemistry based on a Riparian Flow-Concentration

Integration Model. *Hydrology and Earth System Sciences*, *13*(12), 2287–2297. https://doi.org/10.5194/hess-13-2287-2009

Shen, Y., Chapelle, F. H., Strom, E. W., & Benner, R. (2015). Origins and bioavailability of dissolved organic matter in groundwater. *Biogeochemistry*, *122*(1), 61–78. https://doi.org/10.1007/s10533-014-0029-4

Singh, S., Inamdar, S., & Mitchell, M. (2015). Changes in dissolved organic matter (DOM) amount and composition along nested headwater stream locations during baseflow and stormflow. *Hydrological Processes*, *29*(6), 1505–1520. https://doi.org/10.1002/hyp.10286

Singh, S., Inamdar, S., Mitchell, M., & McHale, P. (2014). Seasonal pattern of dissolved organic matter (DOM) in watershed sources: Influence of hydrologic flow paths and autumn leaf fall. *Biogeochemistry*, *118*(1), 321–337. https://doi.org/10.1007/s10533-013-9934-1

Sippel, S., Reichstein, M., Ma, X., Mahecha, M. D., Lange, H., Flach, M., & Frank, D. (2018). Drought, Heat, and the Carbon Cycle: A Review. *Current Climate Change Reports*, *4*(3), 266–286. https://doi.org/10.1007/s40641-018-0103-4

Sleighter, R. L., Cory, R. M., Kaplan, L. A., Abdulla, H. A. N., & Hatcher, P. G. (2014). A coupled geochemical and biogeochemical approach to characterize the bioreactivity of dissolved organic matter from a headwater stream. *Journal of Geophysical Research: Biogeosciences*, *119*(8), 1520–1537. https://doi.org/10.1002/2013JG002600

Soil Classification Working Group. 1998. The Canadian System of Soil Classification, 3rd ed. Agriculture and Agri-Food Canada Publication 1646, 187 pp.

Spence, C., & Woo, M. (2003). Hydrology of subarctic Canadian shield: Soil-filled valleys. *Journal of Hydrology*, *279*(1–4), 151–166. https://doi.org/10.1016/S0022-1694(03)00175-6

Spencer, R. G. M., Butler, K. D., & Aiken, G. R. (2012). Dissolved organic carbon and chromophoric dissolved organic matter properties of rivers in the USA. *Journal of Geophysical Research: Biogeosciences*, *117*(G3). https://doi.org/10.1029/2011JG001928

Spinoni, J., Vogt, J. V., Naumann, G., Barbosa, P., & Dosio, A. (2018). Will drought events become more frequent and severe in Europe? *International Journal of Climatology*, *38*(4), 1718–1736. https://doi.org/10.1002/joc.5291

Stieglitz, M., Shaman, J., McNamara, J., Engel, V., Shanley, J., & Kling, G. W. (2003). An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. *Global Biogeochemical Cycles*, *17*(4). https://doi.org/10.1029/2003GB002041

Stocker, T.F.; Qin, D.; Plattner, G.-K.; Tignor, M.; Allen, S.K.; Boschung, J.; Nauels, A.; Xia, Y.; Bex, V.; Midgley, P.M. Climate change 2013: The physical science basis. In Intergovernmental Panel on Climate Change, Working Group I Contribution to the IPCC Fifth Assessment Report (AR5); Cambridge University Press: New York, NY, USA, 2013.

Strack, M., Waddington, J. M., Bourbonniere, R. A., Buckton, E. L., Shaw, K., Whittington, P., & Price, J. S. (2008). Effect of water table drawdown on peatland dissolved organic carbon export and dynamics. *Hydrological Processes*, *22*(17), 3373–3385. https://doi.org/10.1002/hyp.6931

Strohmeier, S., Knorr, K.-H., Reichert, M., Frei, S., Fleckenstein, J. H., Peiffer, S., & Matzner, E. (2013). Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: Insights from high frequency measurements. *Biogeosciences*, *10*(2), 905–916. https://doi.org/10.5194/bg-10-905-2013

Szkokan-Emilson, E. J., Kielstra, B. W., Arnott, S. E., Watmough, S. A., Gunn, J. M., & Tanentzap, A. J. (2017). Dry conditions disrupt terrestrial–aquatic linkages in northern catchments. *Global Change Biology*, *23*(1), 117–126. https://doi.org/10.1111/gcb.13361

Tank, J. L., Rosi-Marshall, E. J., Griffiths, N. A., Entrekin, S. A., & Stephen, M. L. (2010). A review of allochthonous organic matter dynamics and metabolism in streams. *Journal of the North American Benthological Society*, *29*(1), 118–146. https://doi.org/10.1899/08-170.1

Tank, S. E., Fellman, J. B., Hood, E., & Kritzberg, E. S. (2018). Beyond respiration: Controls on lateral carbon fluxes across the terrestrial-aquatic interface. *Limnology and Oceanography Letters*, *3*(3), 76–88. https://doi.org/10.1002/lol2.10065

Tarnocai, C., Canadell, J. G., Schuur, E. a. G., Kuhry, P., Mazhitova, G., & Zimov, S. (2009). Soil organic carbon pools in the northern circumpolar permafrost region. *Global Biogeochemical Cycles*, *23*(2). https://doi.org/10.1029/2008GB003327

Temnerud, J., & Bishop, K. (2005). Spatial Variation of Streamwater Chemistry in Two Swedish Boreal Catchments: Implications for Environmental Assessment. *Environmental Science & Technology*, *39*(6), 1463–1469. https://doi.org/10.1021/es040045q

Thomas, J. D. (1997). The role of dissolved organic matter, particularly free amino acids and humic substances, in freshwater ecosystems. *Freshwater Biology*, *38*(1), 1–36. https://doi.org/10.1046/j.1365-2427.1997.00206.x

Thompson, S. E., Basu, N. B., Lascurain Jr., J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water Resources Research*, *47*(10). https://doi.org/10.1029/2010WR009605

Thurman, E. M. (1985). Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr W Junk, Dordrecht, The Netherlands.

Tiwari, T., Lidman, F., Laudon, H., Lidberg, W., & Ågren, A. M. (2017). GIS-based prediction of stream chemistry using landscape composition, wet areas, and hydrological flow pathways. *Journal of Geophysical Research: Biogeosciences*, *122*(1), 65–79. https://doi.org/10.1002/2016JG003399

Tiwari, T., Laudon, H., Beven, K., & Ågren, A. M. (2014). Downstream changes in DOC: Inferring contributions in the face of model uncertainties. *Water Resources Research*, *50*(1), 514–525. https://doi.org/10.1002/2013WR014275

Tiwari, T., Sponseller, R. A., & Laudon, H. (2019). Contrasting responses in dissolved organic carbon to extreme climate events from adjacent boreal landscapes in Northern Sweden. *Environmental Research Letters*, *14*(8), 084007. https://doi.org/10.1088/1748-9326/ab23d4

Tiwari, T., Sponseller, R. A., & Laudon, H. (2022). The emerging role of drought as a regulator of dissolved organic carbon in boreal landscapes. *Nature Communications*, *13*(1), Article 1. https://doi.org/10.1038/s41467-022-32839-3

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack, J. M., Overholt, E., … Weyhenmeyer, G. A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, *54*(6part2), 2298–2314. https://doi.org/10.4319/lo.2009.54.6_part_2.2298

Trumbore, S. E., & Harden, J. W. (1997). Accumulation and turnover of carbon in organic and mineral soils of the BOREAS northern study area. *Journal of Geophysical Research: Atmospheres*, *102*(D24), 28817–28830. https://doi.org/10.1029/97JD02231

Tugulea, A.-M., Aranda-Rodriguez, R., Bérubé, D., Giddings, M., Lemieux, F., Hnatiw, J., Dabeka, L., & Breton, F. (2018). The influence of precursors and treatment process on the formation of Iodo-THMs in Canadian drinking water. *Water Research*, *130*, 215–223. https://doi.org/10.1016/j.watres.2017.11.055

Tunaley, C., Tetzlaff, D., Lessels, J., & Soulsby, C. (2016). Linking high-frequency DOC dynamics to the age of connected water sources. *Water Resources Research*, *52*(7), 5232–5247. https://doi.org/10.1002/2015WR018419

van Hees, P. A. W., Jones, D. L., Nyberg, L., Holmström, S. J. M., Godbold, D. L., & Lundström, U. S. (2005). Modelling low molecular weight organic acid dynamics in forest soils. *Soil Biology and Biochemistry*, *37*(3), 517–531. https://doi.org/10.1016/j.soilbio.2004.08.014

Valinia, S., Englund, G., Moldan, F., Futter, M. N., Köhler, S. J., Bishop, K., & Fölster, J. (2014). Assessing anthropogenic impact on boreal lakes with historical fish species distribution data and hydrogeochemical modeling. *Global Change Biology*, *20*(9), 2752–2764. https://doi.org/10.1111/gcb.12527

Vannote, R. L., Minshall, G. W., Cummins, K. W., Sedell, J. R., & Cushing, C. E. (1980). The River Continuum Concept. *Canadian Journal of Fisheries and Aquatic Sciences*, *37*(1), 130–137. https://doi.org/10.1139/f80-017

Vidon, P., Allan, C., Burns, D., Duval, T. P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., & Sebestyen, S. (2010). Hot Spots and Hot Moments in Riparian Zones: Potential for Improved Water Quality Management. *JAWRA Journal of the American Water Resources Association*, *46*(2), 278–298. https://doi.org/10.1111/j.1752-1688.2010.00420.x

Voss, B. M., Peucker-Ehrenbrink, B., Eglinton, T. I., Spencer, R. G. M., Bulygina, E., Galy, V., Lamborg, C. H., Ganguli, P. M., Montluçon, D. B., Marsh, S., Gillies, S. L., Fanslau, J., Epp, A., & Luymes, R. (2015). Seasonal hydrology drives rapid shifts in the flux and composition of dissolved and particulate organic carbon and major and trace ions in the Fraser River, Canada. *Biogeosciences*, *12*(19), 5597–5618. https://doi.org/10.5194/bg-12-5597-2015

Waddington, J. M., & Roulet, N. T. (1997). Groundwater flow and dissolved carbon movement in a boreal peatland. *Journal of Hydrology*, *191*(1), 122–138. https://doi.org/10.1016/S0022-1694(96)03075-2

Waddington, J. M., & Roulet, N. T. (2000). Carbon balance of a boreal patterned peatland. *Global Change Biology*, *6*(1), 87–97. https://doi.org/10.1046/j.1365-2486.2000.00283.x

Wagener, T., Sivapalan, M., Troch, P., & Woods, R. (2007). Catchment Classification and Hydrologic Similarity. *Geography Compass*, *1*(4), 901–931. https://doi.org/10.1111/j.1749-8198.2007.00039.x

Walker, C. M., King, R. S., Whigham, D. F., & Baird, S. J. (2012). Landscape and Wetland Influences on Headwater Stream Chemistry in the Kenai Lowlands, Alaska. *Wetlands*, *32*(2), 301–310. https://doi.org/10.1007/s13157-011-0260-x

Wardinski, K. M., Hotchkiss, E. R., Jones, C. N., McLaughlin, D. L., Strahm, B. D., & Scott, D. T. (2022). Water-Soluble Organic Matter From Soils at the Terrestrial-Aquatic Interface in Wetland-Dominated Landscapes. *Journal of Geophysical Research: Biogeosciences*, *127*(9), e2022JG006994. https://doi.org/10.1029/2022JG006994

Webb, J. R., Santos, I. R., Maher, D. T., & Finlay, K. (2019). The Importance of Aquatic Carbon Fluxes in Net Ecosystem Carbon Budgets: A Catchment-Scale Review. *Ecosystems*, *22*(3), 508–527. https://doi.org/10.1007/s10021-018-0284-7

Webster, K. L., & McLaughlin, J. W. (2010). Importance of the Water Table in Controlling Dissolved Carbon along a Fen Nutrient Gradient. *Soil Science Society of America Journal*, *74*(6), 2254–2266. https://doi.org/10.2136/sssaj2009.0111

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. *Environmental Science & Technology*, *37*(20), 4702–4708. https://doi.org/10.1021/es030360x

Wen, H., Perdrial, J., Abbott, B. W., Bernal, S., Dupas, R., Godsey, S. E., Harpold, A., Rizzo, D., Underwood, K., Adler, T., Sterle, G., & Li, L. (2020). Temperature controls production but hydrology regulates export of dissolved organic carbon at the catchment scale. *Hydrology and Earth System Sciences*, *24*(2), 945–966. https://doi.org/10.5194/hess-24-945-2020

Werner, B. J., Musolff, A., Lechtenfeld, O. J., de Rooij, G. H., Oosterwoud, M. R., & Fleckenstein, J. H. (2019). High-frequency measurements explain quantity and quality of dissolved organic carbon mobilization in a headwater catchment. *Biogeosciences*, *16*(22), 4497–4516. https://doi.org/10.5194/bg-16-4497-2019

Werner, B. J., Lechtenfeld, O. J., Musolff, A., de Rooij, G. H., Yang, J., Gründling, R., Werban, U., & Fleckenstein, J. H. (2021). Small-scale topography explains patterns and dynamics of dissolved organic carbon exports from the riparian zone of a temperate, forested catchment. *Hydrology and Earth System Sciences*, *25*(12), 6067–6086. https://doi.org/10.5194/hess-25-6067-2021

Wickland, K. P., Neff, J. C., & Aiken, G. R. (2007). Dissolved Organic Carbon in Alaskan Boreal Forest: Sources, Chemical Characteristics, and Biodegradability. *Ecosystems*, *10*(8), 1323–1340. https://doi.org/10.1007/s10021-007-9101-4

Wiegner, T. N., Tubal, R. L., & MacKenzie, R. A. (2009). Bioavailability and export of dissolved organic matter from a tropical river during base- and stormflow conditions. *Limnology and Oceanography*, *54*(4), 1233–1242. https://doi.org/10.4319/lo.2009.54.4.1233

Williamson, C. E., Morris, D. P., Pace, M. L., & Olson, O. G. (1999). Dissolved organic carbon and nutrients as regulators of lake ecosystems: Resurrection of a more integrated paradigm. *Limnology and Oceanography*, *44*(3part2), 795–803. https://doi.org/10.4319/lo.1999.44.3_part_2.0795

Williamson, C. E., Dodds, W., Kratz, T. K., & Palmer, M. A. (2008). Lakes and streams as sentinels of environmental change in terrestrial and atmospheric processes. *Frontiers in Ecology and the Environment*, *6*(5), 247–254. https://doi.org/10.1890/070140

Winterdahl, M., Erlandsson, M., Futter, M. N., Weyhenmeyer, G. A., & Bishop, K. (2014). Intra-annual variability of organic carbon concentrations in running waters: Drivers along a climatic gradient. *Global Biogeochemical Cycles*, *28*(4), 451–464. https://doi.org/10.1002/2013GB004770

Winterdahl, M., Futter, M., Köhler, S., Laudon, H., Seibert, J., & Bishop, K. (2011). Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. *Water Resources Research*, *47*(8). https://doi.org/10.1029/2010WR010235

Winterdahl, M., Laudon, H., Lyon, S. W., Pers, C., & Bishop, K. (2016). Sensitivity of stream dissolved organic carbon to temperature and discharge: Implications of future climates. *Journal of Geophysical Research: Biogeosciences*, *121*(1), 126–144. https://doi.org/10.1002/2015JG002922

Wolock, D. M., Hornberger, G. M., & Musgrove, T. J. (1990). Topographic effects on flow path and surface water chemistry of the Llyn Brianne catchments in Wales. *Journal of Hydrology*, *115*(1), 243–259. https://doi.org/10.1016/0022-1694(90)90207-E

Worrall, F., Gibson, H. S., & Burt, T. P. (2008). Production vs. Solubility in controlling runoff of DOC from peat soils – The use of an event analysis. *Journal of Hydrology*, *358*(1), 84–95. https://doi.org/10.1016/j.jhydrol.2008.05.037

Wu, J., Yao, H., Yuan, X., & Lin, B. (2022). Dissolved organic carbon response to hydrological drought characteristics: Based on long-term measurements of headwater streams. *Water Research*, *215*, 118252. https://doi.org/10.1016/j.watres.2022.118252

Wymore, A. S., Johnes, P. J., Bernal, S., Brookshire, E. N. J., Fazekas, H. M., Helton, A. M., Argerich, A., Barnes, R. T., Coble, A. A., Dodds, W. K., Haq, S., Johnson, S. L., Jones, J. B., Kaushal, S. S., Kortelainen, P., López-Lloreda, C., Rodríguez-Cardona, B. M., Spencer, R. G. M., Sullivan, P. L., … McDowell, W. H. (2021). Gradients of Anthropogenic Nutrient Enrichment Alter N Composition and DOM Stoichiometry in Freshwater Ecosystems. *Global Biogeochemical Cycles*, *35*(8), e2021GB006953. https://doi.org/10.1029/2021GB006953

Xenopoulos, M. A., Barnes, R. T., Boodoo, K. S., Butman, D., Catalán, N., D'Amario, S. C., Fasching, C., Kothawala, D. N., Pisani, O., Solomon, C. T., Spencer, R. G. M., Williams, C. J., & Wilson, H. F. (2021). How humans alter dissolved organic matter composition in freshwater: Relevance for the Earth's biogeochemistry. *Biogeochemistry*, *154*(2), 323–348. https://doi.org/10.1007/s10533-021-00753-3

Yates, C. A., Johnes, P. J., Owen, A. T., Brailsford, F. L., Glanville, H. C., Evans, C. D., Marshall, M. R., Jones, D. L., Lloyd, C. E. M., Jickells, T., & Evershed, R. P. (2019). Variation in dissolved organic matter (DOM) stoichiometry in U.K. freshwaters: Assessing the influence of land cover and soil C:N ratio on DOM composition. *Limnology and Oceanography*, *64*(6), 2328–2340. https://doi.org/10.1002/lno.11186

Yu, Z., Loisel, J., Brosseau, D. P., Beilman, D. W., & Hunt, S. J. (2010). Global peatland dynamics since the Last Glacial Maximum. *Geophysical Research Letters*, *37*(13). https://doi.org/10.1029/2010GL043584

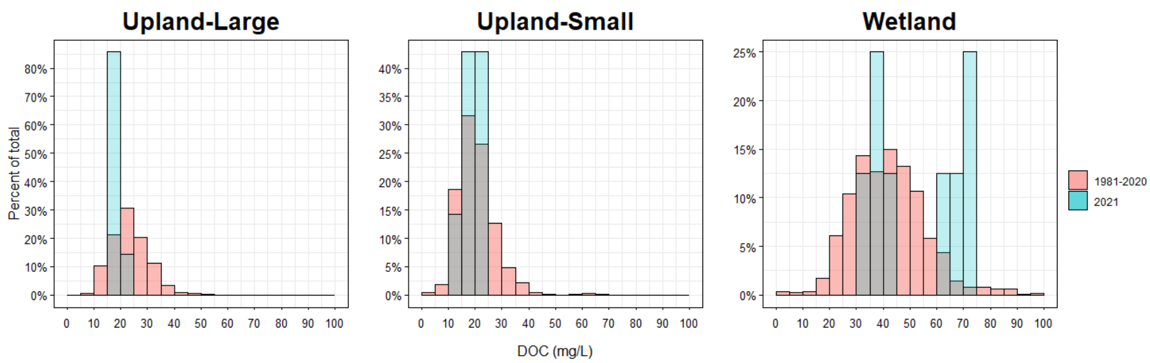
Zarnetske, J. P., Bouda, M., Abbott, B. W., Saiers, J., & Raymond, P. A. (2018). Generality of Hydrologic Transport Limitation of Watershed Organic Carbon Flux Across Ecoregions of the United States. *Geophysical Research Letters*, *45*(21), 11,702-11,711. https://doi.org/10.1029/2018GL080005

Zimmer, M. A., & McGlynn, B. L. (2018). Lateral, Vertical, and Longitudinal Source Area Connectivity Drive Runoff and Carbon Export Across Watershed Scales. *Water Resources Research*, *54*(3), 1576–1598. https://doi.org/10.1002/2017WR021718

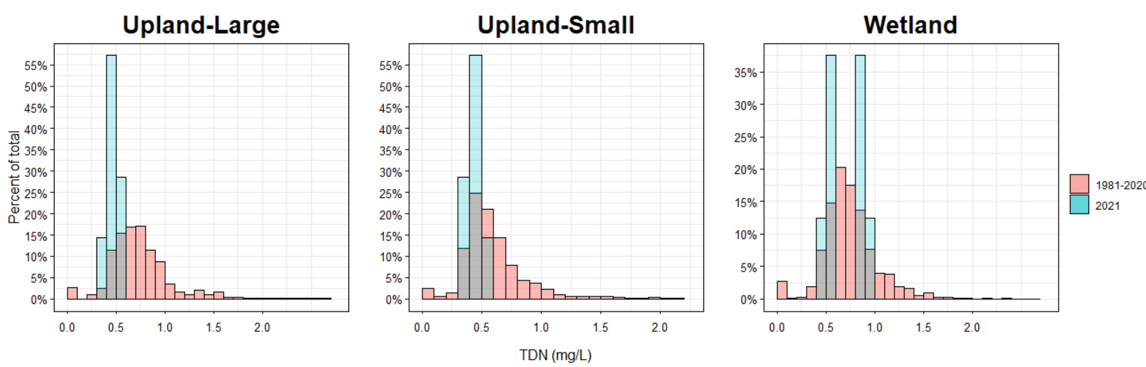
Zsolnay, Á. (2003). Dissolved organic matter: Artefacts, definitions, and functions. *Geoderma*, *113*(3), 187–209. https://doi.org/10.1016/S0016-7061(02)00361-0

7. Supplemental materials

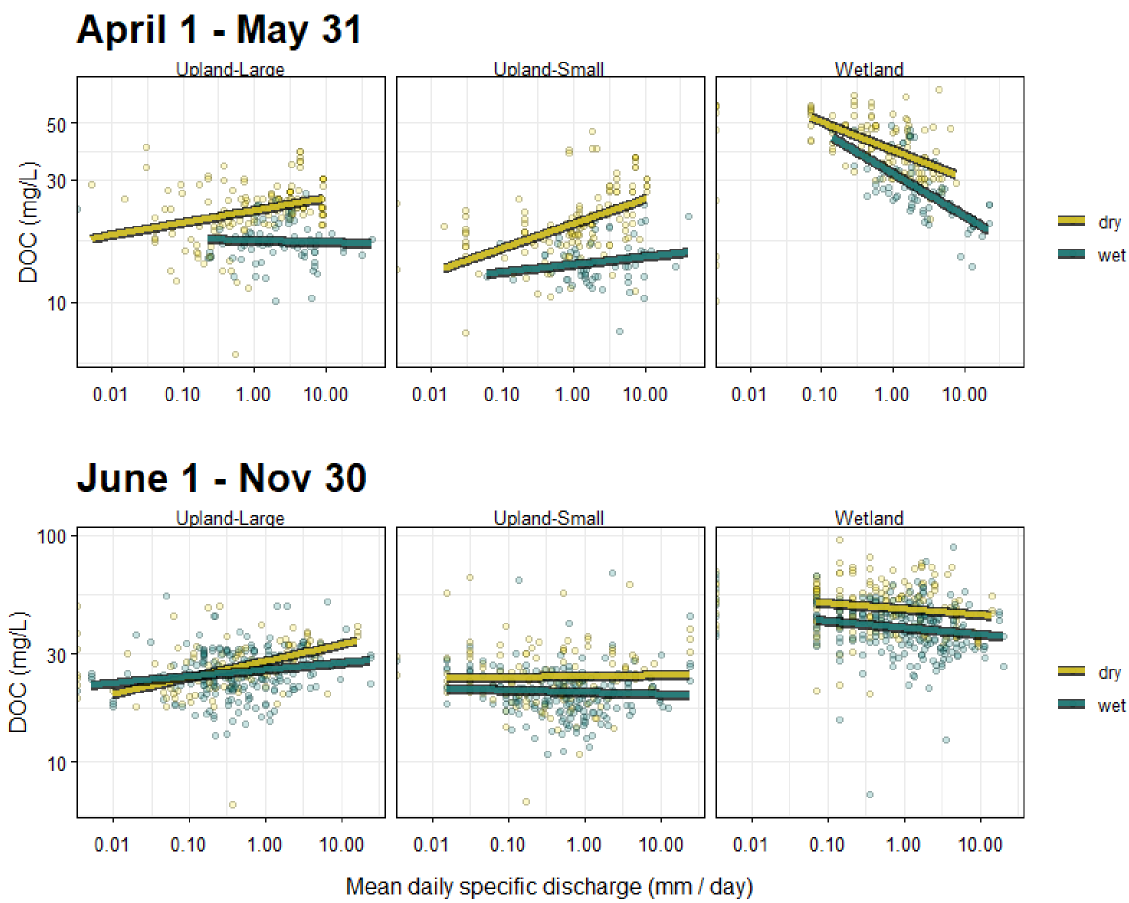
7.1 Supplemental Figures



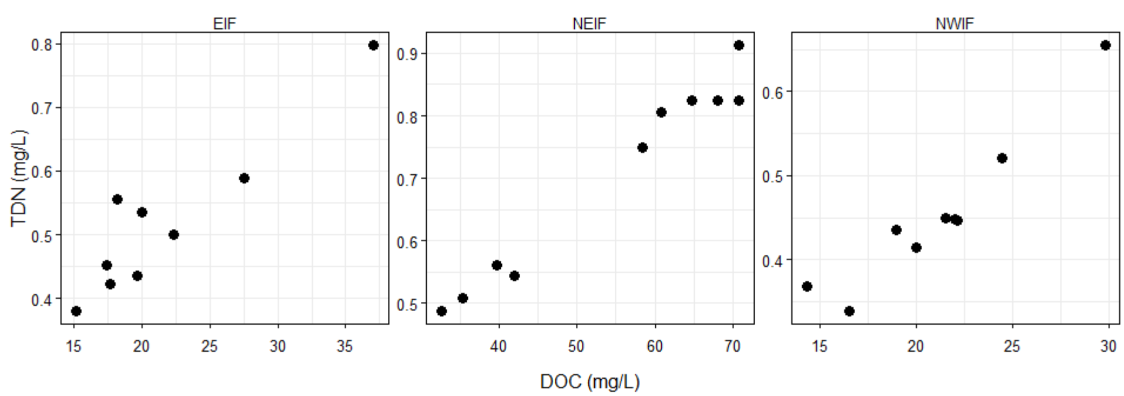
Supplemental Figure 1: Histograms of stream DOC concentrations from 1981-2020 and 2021 water years.



Supplemental Figure 2: Histograms of stream TDN concentrations from 1981-2020 and 2021 water years.



Supplemental Figure 3: Historical c-Q relationships during and after the snowmelt period



Supplemental Figure 4: DOC and TDN concentration in 2021

7.2 Supplemental Tables

Supplemental Table 1: Catchment characteristics

Catchment	Variable	Unit	Mean	SD	Range	Min	Max
Upland-Large	Elevation	m.a.s..l.	428	15.5	66.6	391	457
Upland-Small	Elevation	m.a.s..l.	420	12.2	56.6	392	448
Wetland-dominated	Elevation	m.a.s..l.	420	10.3	43.7	406	450
Upland-Large	NDVI		0.457	0.116	0.7	0	0.699
Upland-Small	NDVI		0.485	0.112	0.761	0	0.721
Wetland-dominated	NDVI		0.467	0.093	0.615	0.077	0.692
Upland-Large	Slope	degrees	8.57	7.51	52.8	0	52.8
Upland-Small	Slope	degrees	6.83	5.63	44.4	0	44.4
Wetland-dominated	Slope	degrees	8.31	7.91	66.9	0	66.9
Upland-Large	TWI		3.68	1.01	7.23	0	7.23
Upland-Small	TWI		3.79	0.904	7.48	0	7.48
Wetland-dominated	TWI		3.87	1.47	7.94	0	7.94

Supplemental Table 2: Comparing DOC and TDN from 2021 to 1981-2020 stream data.

Analyte	Year	Mean	SD	Min	Max
Upland-Large					
DOC (mg/L)	1971-2020	23.3	7.18	0.06	73.1
DOC (mg/L)	2021	18.6	2.3	15.1	22.4
TDN (mg/L)	1971-2020	0.785	0.475	0	4.78
TDN (mg/L)	2021	0.469	0.063	0.381	0.555
Wetland-dominated					
DOC (mg/L)	1971-2020	41.9	13.8	0.06	98.5
DOC (mg/L)	2021	53	17	32.6	70.9
TDN (mg/L)	1971-2020	0.746	0.277	0	2.32
TDN (mg/L)	2021	0.686	0.176	0.488	0.913
Upland-Small					
DOC (mg/L)	1971-2020	20.4	7.11	0.06	67.9
DOC (mg/L)	2021	19.8	3.5	14.3	24.4
TDN (mg/L)	1971-2020	0.606	0.315	0	2.63
TDN (mg/L)	2021	0.424	0.059	0.339	0.521

Supplemental Table 3: Linear regression values for historical c-Q relationships (log10 DOC x log10 Q) among dry and wet years spanning from 1981-2021.

Water year wetness	P Value	R squared	Slope	Intercept
Upland-Large				
Dry	0	0.079	0.046	1.39
Wet	0.017	0.018	-0.024	1.35
Upland-Small				
Dry	0.004	0.032	0.033	1.35
Wet	0.001	0.039	-0.035	1.27
Wetland-dominated				
Dry	0	0.086	-0.054	1.64
Wet	0	0.12	-0.081	1.56

Supplemental Table 4: Linear regression values for historical c-Q relationships (log10 DOC x log10 Q) among dry and wet years from 1981-2021 during the snowmelt period.

Water year wetness	P Value	R squared	Slope	Intercept
Upland-Large				
Dry	0	0.098	0.048	1.36
Wet	0.703	0.002	-0.007	1.24
Upland-Small				
Dry	0	0.246	0.096	1.31
Wet	0.107	0.039	0.03	1.15
Wetland-dominated				
Dry	0	0.319	-0.11	1.6
Wet	0	0.467	-0.165	1.51

Supplemental Table 5: Linear regression model values for historical c-Q relationships among dry and wet years from 1981-2021 after the snowmelt period.

Water year wetness	P Value	R squared	Slope	Intercept
Upland-Large				
Dry	0	0.175	0.073	1.44
Wet	0.005	0.034	0.03	1.41
Upland-Small				
Dry	0.77	0.001	0.005	1.38
Wet	0.413	0.003	-0.009	1.31
Wetland-dominated				
Dry	0.051	0.023	-0.025	1.67
Wet	0.033	0.02	-0.029	1.59

Supplemental Table 6: Linear regression values for historical c-Q relationships using antecedent flow (log10 DOC x log10 AQ) among dry and wet years from 1981-2021.

Water year wetness	Antecedent flow	P Value	R squared	Slope	Intercept
Upland-Large					
Dry	7-day	0.009	0.026	0.027	1.37
Dry	14-day	0.269	0.005	0.012	1.37
Dry	21-day	0.631	0.001	0.005	1.38
Dry	28-day	0.984	0	0	1.38
Wet	7-day	0.003	0.028	-0.032	1.38
Wet	14-day	0	0.043	-0.048	1.4
Wet	21-day	0	0.048	-0.055	1.42
Wet	28-day	0	0.041	-0.054	1.43
Upland-Small					
Dry	7-day	0.857	0	0.002	1.34
Dry	14-day	0.232	0.006	-0.014	1.35
Dry	21-day	0.078	0.012	-0.02	1.36
Dry	28-day	0.04	0.016	-0.023	1.37
Wet	7-day	0	0.116	-0.062	1.32
Wet	14-day	0	0.158	-0.077	1.35
Wet	21-day	0	0.179	-0.086	1.38
Wet	28-day	0	0.165	-0.086	1.4
Wetland-dominated					
Dry	7-day	0	0.305	-0.094	1.71
Dry	14-day	0	0.337	-0.103	1.74
Dry	21-day	0	0.332	-0.103	1.76
Dry	28-day	0	0.317	-0.1	1.76
Wet	7-day	0	0.245	-0.125	1.68
Wet	14-day	0	0.307	-0.15	1.75
Wet	21-day	0	0.326	-0.156	1.78
Wet	28-day	0	0.339	-0.175	1.84

Supplemental Table 7: Linear regression values for historical c-Q relationships using antecedent flow among dry and wet years from 1981-2021 during snowmelt.

Water year wetness	Antecedent flow	P Value	R squared	Slope	Intercept
Upland-Large					
Dry	7-day	0.003	0.055	0.038	1.33
Dry	14-day	0.161	0.012	0.019	1.34
Dry	21-day	0.645	0.001	0.006	1.35
Dry	28-day	0.952	0	-0.001	1.36
Wet	7-day	0.08	0.037	-0.031	1.28
Wet	14-day	0.037	0.053	-0.039	1.29
Wet	21-day	0.03	0.057	-0.04	1.3
Wet	28-day	0.036	0.053	-0.037	1.3
Upland-Small					
Dry	7-day	0.001	0.08	0.049	1.27
Dry	14-day	0.021	0.04	0.034	1.27
Dry	21-day	0.104	0.02	0.023	1.28
Dry	28-day	0.279	0.009	0.015	1.29
Wet	7-day	0.79	0.001	-0.005	1.16
Wet	14-day	0.415	0.01	-0.016	1.18
Wet	21-day	0.315	0.016	-0.019	1.19
Wet	28-day	0.281	0.018	-0.02	1.19
Wetland-dominated					
Dry	7-day	0	0.6	-0.132	1.69
Dry	14-day	0	0.64	-0.137	1.73
Dry	21-day	0	0.622	-0.133	1.75
Dry	28-day	0	0.592	-0.129	1.75
Wet	7-day	0	0.594	-0.181	1.66
Wet	14-day	0	0.62	-0.182	1.71
Wet	21-day	0	0.622	-0.178	1.73
Wet	28-day	0	0.613	-0.173	1.74

Supplemental Table 8: Linear regression values for historical c-Q relationships using antecedent flow among dry and wet years from 1981-2021 after snowmelt.

Water year wetness	Antecedent flow	P Value	R squared	Slope	Intercept
Upland-Large					
Dry	7-day	0.001	0.1	0.059	1.4
Dry	14-day	0.006	0.071	0.05	1.39
Dry	21-day	0.008	0.065	0.051	1.38
Dry	28-day	0.025	0.048	0.044	1.38
Wet	7-day	0.018	0.024	0.027	1.39
Wet	14-day	0.16	0.009	0.02	1.38
Wet	21-day	0.695	0.001	0.006	1.39
Wet	28-day	0.997	0	0	1.39
Upland-Small					
Dry	7-day	0.048	0.031	-0.034	1.39
Dry	14-day	0	0.099	-0.065	1.43
Dry	21-day	0	0.135	-0.078	1.45
Dry	28-day	0	0.153	-0.087	1.47
Wet	7-day	0.002	0.047	-0.036	1.33
Wet	14-day	0	0.101	-0.056	1.36
Wet	21-day	0	0.148	-0.071	1.39
Wet	28-day	0	0.157	-0.078	1.42
Wetland-dominated					
Dry	7-day	0	0.206	-0.072	1.72
Dry	14-day	0	0.251	-0.084	1.76
Dry	21-day	0	0.263	-0.088	1.77
Dry	28-day	0	0.278	-0.091	1.79
Wet	7-day	0	0.118	-0.078	1.66
Wet	14-day	0	0.182	-0.108	1.72
Wet	21-day	0	0.217	-0.12	1.76
Wet	28-day	0	0.254	-0.15	1.83

Supplemental Table 9: Mean, SD, Min, and Max of soil leachate DOM quantity and quality in 2021.

Analyte	Mean	SD	Min	Max
Upland-Large				
DOC	6.72	4.79	2.19	18.8
TDN	1.2	1.17	0.141	3.86
SUVA	2.14	0.429	1.39	2.82
S275-295	0.015	0.001	0.013	0.016
Sr	0.826	0.043	0.75	0.897
BIX	0.481	0.074	0.268	0.641
FI	1.11	0.088	0.937	1.24
Upland-Small				
DOC	5.78	3.63	2.49	15.9
TDN	0.895	1.12	0.158	5.26
SUVA	2.05	0.535	1.09	2.94
S275-295	0.015	0.001	0.012	0.017
Sr	0.827	0.076	0.671	1.02
BIX	0.467	0.1	0.136	0.59
FI	1.1	0.1	0.904	1.25
Wetland-dominated				
DOC	29.33	13.9	3.51	50.7
TDN	3.6	1.57	0.149	5.5
SUVA	2.89	0.499	2.03	3.8
S275-295	0.012	0.001	0.011	0.013
Sr	0.702	0.043	0.636	0.803
BIX	0.447	0.059	0.31	0.555
FI	1.02	0.043	0.959	1.08

Supplemental Table 10: Mean, SD, Min, and Max of streamwater DOM quantity and quality in 2021.

analyte	mean	sd	min	max
Upland-Large				
DOC	21.6	6.8	15.1	37.1
TDN	0.519	0.124	0.381	0.797
SUVA	3.18	0.102	3.02	3.37
S275-295	0.013	0	0.012	0.013
Sr	0.723	0.009	0.71	0.737
BIX	0.502	0.032	0.434	0.543
FI	1.15	0.02	1.12	1.17
Upland-Small				
DOC	21.1	4.5	14.3	29.8
TDN	0.453	0.092	0.339	0.655
SUVA	2.94	0.154	2.68	3.15
S275-295	0.013	0.001	0.013	0.014
Sr	0.735	0.016	0.713	0.756
BIX	0.523	0.041	0.46	0.595
FI	1.17	0.038	1.13	1.25
Wetland-dominated				
DOC	54.3	15.3	32.6	70.9
TDN	0.704	0.16	0.488	0.913
SUVA	3.01	0.175	2.79	3.2
S275-295	0.013	0	0.012	0.013
Sr	0.695	0.011	0.677	0.711
BIX	0.489	0.018	0.468	0.534
FI	1.1	0.024	1.06	1.15