Mobilization of soil dissolved organic matter in mesic boreal forests of Newfoundland and Labrador, Canada

by

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Abstract

The mobilization of soil dissolved organic matter (DOM) distributes carbon and nutrients within ecosystems and links terrestrial to aquatic environments. As a hydrologically and biogeochemically mediated flux, DOM mobilization encapsulates a number of interacting ecological processes. This presents a major challenge for identifying the main drivers of DOM mobilization at different spatial and temporal scales. In this thesis, I use two mesic boreal forest research platforms to investigate the drivers of DOM mobilization from the organic horizon at different spatiotemporal scales. Using an experimentally harvested site, I show that total annual DOC flux from O horizons is due to both vertical and lateral flow, and was 30% percent greater in the harvested plots with significantly reduced organic horizons. Additionally, the C:N of DOM and absorbance characteristics of samples in both treatments demonstrated a stronger control of season over harvesting on the composition of DOM mobilized. One of the most significant of these seasonal controls was the snowpack insulation throughout winter. The lower C:N, higher $\text{SUVA}_{254\text{nm}}$ and lower molecular weight of chromophoric DOM mobilized during winter and snowmelt indicates relatively more decomposed DOM, compared to that mobilized in summer and autumn. This shows that the decomposition of soil organic matter underneath a consistently deep snowpack is a key determinant of the composition of DOM mobilized from O horizons during winter and the hydrologically significant snowmelt period. Additionally, I show that air temperature and snowpack duration best explain DOM mobilization dynamics both interannually within boreal sites and among boreal forest sites along a climate transect. This suggests that air temperature indirectly affects DOC mobilization through a direct control on snowpack season length in these forests. Furthermore, climate influenced differences in ecosystem properties such as organic horizon thickness, moss coverage and stand density, may additionally influence DOM mobilization through a direct control on soil hydrology. These results enhance our understanding of the relationship between boreal forest soil organic matter and soil DOM and the potential impacts of climate change on soil organic matter losses as DOM, contributing to a predictive understanding of forest C and nutrient distribution and the potential effect on aquatic environments.

General Summary

Boreal forests contain more carbon (C) in the soil than in trees, most of which exists close to the surface of the forest floor in a layer called the organic horizon. Boreal forests are currently a net sink of C, meaning that they sequester more C than they release to the atmosphere. Recently, it was discovered that accurate measurement of the boreal forest C sink requires inclusion of soil organic matter that is dissolved and flushed from forests during precipitation events. This "soil to stream" export can sometimes be large enough to flip C balance estimates from a net C sink to a net C source. Understanding the dominant controls on this export is challenging because it is influenced by many interacting biological, chemical, geological and hydrological processes. In this thesis, I investigated the dominant controls on soil dissolved organic matter (soil DOM) losses in eastern boreal forests of Canada, and tested the effects of two anthropogenic disturbances: tree harvesting and climate change. I found that more soil DOM is lost from harvested plots because more water is able to reach and move through the soil in the absence of a tree canopy. I also found that temperature exerts a secondary control, where warm soils with a lot of water moving through them can lose more DOM than cooler soils with a lot of water moving through them. Secondly, I used specific absorbance metrics in combination with the ratio between C and nitrogen (N) in DOM to examine how the composition of soil DOM changes with respect to season and harvesting. I found that season exerted a greater control on the composition of DOM than the effect of harvesting. One of the most significant effects of season was the snowpack, which insulated the soil during winter, controlling the composition of winter and snowmelt DOM through the maintenance of microbial decomposition underneath the snowpack. Thirdly, I found that air temperature and the duration of snow-cover largely explained annual soil DOM losses over multiple years and among forest sites. Together, these results suggest that the movement of soil DOM in the eastern boreal forest is particularly vulnerable to the changing snowpack regime, as well as combined increases in precipitation and air temperature.

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Coauthorship Statement

I had the pleasure of collaborating with many extraordinary scientists on this work. This was the highlight of my graduate school experience. Below are the details of our work together and individual contributions to the manuscript chapters of this thesis (this information is also provided on the title page of each manuscript chapter).

Chapter 2: Dissolved organic carbon mobilized from organic horizons of mature and harvested black spruce plots in a mesic boreal region

Authors: Keri L. Bowering, Kate A. Edwards, Karen Prestegaard, Xinbiao Zhu, and Susan E. Ziegler

KAE and SEZ conceptualized the study with input from KLB. KB and KAE selected the research site, designed the lysimeters and planned their installation as well as installation of all environmental monitoring equipment. KB collected and analysed the lysimeter, environmental monitoring and soil properties data. XZ contributed the soil respiration data and analysis. KP contributed soil hydrology data and interpretations. KB prepared the paper, with editing from SEZ and KAE and further contributions on final drafts from XZ and KP.

Chapter 3: Seasonal controls override the effects of forest harvesting on the composition of dissolved organic matter mobilized from boreal forest soil organic horizons

Authors: Keri L. Bowering, Kate A. Edwards, Susan E. Ziegler

KAE and SEZ conceptualized the study with input from KLB. KLB and KAE designed the lysimeters and planned their installation as well as installation of all environmental monitoring equipment. KLB collected and analysed the lysimeter, environmental monitoring and soil properties data. KLB prepared the paper, with editing from SEZ and KAE

Chapter 4: Dissolved organic carbon mobilization across a climate transect of mesic boreal forests is explained by coupled air temperature and snowpack duration

Authors: Keri L. Bowering, Kate A. Edwards, Yolanda F. Wiersma, Sharon A. Billings, Jamie Warren, Andrea Skinner, and Susan E. Ziegler

KAE, SAB and SEZ designed the study with instrumentation input from JW and AS. AS and KAE collected designed and maintained the sampling regime. JW performed laboratory analyses. KLB and KAE analyzed the data, with input from SEZ. YFW provided pertinent statistical advice. KLB prepared the manuscript with editing by KAE, SEZ, SAB and YFW.

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Chapter 1

Introduction

1.1 Background

1.1.1 Carbon and nutrient mobilization from terrestrial to aquatic systems

The mobilization of soil dissolved organic matter (DOM) distributes carbon and nutrients within ecosystems and links the carbon and nutrient cycles of terrestrial systems to aquatic systems. It is a hydrologically and biogeochemically mediated flux that therefore encapsulates a number of interacting ecological processes. These interactions present a major challenge for identifying the main drivers of DOM mobilization at different spatial and temporal scales (Jansen et al., 2014). For instance, water movement is necessary to the mobilization of DOM, however, how catchments receive and transport precipitation depends on local vegetation cover, soil type, geology, and climate. Precipitation and soil moisture are also important to primary productivity and decomposition rates that determine the accumulation and persistence of soil organic matter (Schmidt et al., 2011; Oquist et al., 2014), and soil organic matter is the predominant source of DOM in headwaters. The response of runoff and streamflow to precipitation can vary among catchments even within a climate region (Teutschbein et al., 2015). Therefore, spatial variations in the mobilization of soil DOM, and controls on the contribution of soil DOM to aquatic systems is expected but not well understood.

Boreal forests account for 27% of the global forest area (FAO and UNEP, 2020) and contain at least 50% of the global forest carbon stock (DeLuca and Boisvenue, 2012). Boreal forests contain more carbon in the soil than in plant biomass, in part, because of the temperature limitation on decomposition which results in the large buildup of soil carbon in boreal forests compared to tropical and temperate forests (Malhi et al., 1999). Boreal forests are also experiencing stronger climate warming than the global average, and one concerning feedback of warming is the release of a significant proportion of the boreal soil carbon reservoir as carbon dioxide (CO_2) to the atmosphere (Hoegh-Guldberg et al., 2018). Losses of soil organic matter are also possible through mobilization of soil DOM, although whether DOM constitutes a significant mass loss of soil organic matter compared to CO_2 losses is unclear. Recent “browning of waters” in northern latitudes (Roulet and Moore, 2006) as a result of increased dissolved organic carbon (DOC) and iron concentrations in streams, rivers, and lakes suggests that DOM losses can be ecologically significant, stimulating research focussed on understanding the controls on the export of DOC from terrestrial to aquatic (T-A) systems. Initially, browning was explained by rising temperatures (Freeman et al., 2001), however, Tranvik and Jansson (2002) argued that the effect of rising temperatures on DOC mobilization is dependent on the direction of precipitation change. The successful mitigation of acid rain provides another explanation for increased DOC concentrations because decreased sulfate concentrations and increased pH of rain mobilizes more terrestrial carbon (Evans et al., 2005; Monteith et al., 2007). The effect of reduced acid deposition may further be exacerbated by a wetter climate (de Wit et al., 2016). Currently, the combination of environmental conditions (i.e., climate change and weather patterns) and acid deposition, in addition to land cover and land use change contribute to our understanding of browning, but the relative importance of each of these principal drivers are spatially variable (Kritzberg et al., 2020).

Lateral fluxes of DOM from terrestrial to aquatic (T-A) systems are an important yet underrepresented component of the global carbon cycle (Cole et al., 2007, Battin et al., 2009, Tranvik et al., 2009, Kindler et al., 2011). The underrepresentation of the T-A flux is reflected in the fact that the Intergovernmental Panel on Climate Change (IPCC) did not include this flux in the global carbon cycle until the Second Assessment report (Denman et al., 2007). Lateral losses of terrestrial DOM can be thought of as an aquatic "offset" on terrestrial net ecosystem productivity (NEP) estimates. The spatial variations and controls on the magnitude of the T-A "offset" on terrestrial NEP, however, are not well known but may explain the uncertainty of the land-atmosphere carbon flux relative to that modeled for the ocean-atmosphere (Friedlingstein et al. 2014). The significance of the T-A flux varies across ecosystems and may have greatest offset potential in systems with low NEP (Webb et al., 2019). Interestingly, Webb et al. (2019) identify precipitation as an important driver of both NEP and aquatic fluxes. While NEP responds to annual variations in precipitation, aquatic carbon fluxes are less responsive likely because they are influenced by the longer-term effects of precipitation on ecosystem structure (i.e. vegetation cover and soil carbon stocks). This is an example of interacting processes important to the mobilization of DOM that operate at different scales and remains an important area for future work.

1.1.2 The role of soil organic horizons in boreal catchment hydrology and biogeochemistry

Podzols cover 463 million hectares of the global land surface and are the predominant soil type of cool, wet temperate and boreal forests (Sanborn et al., 2011). They are, in part, characterized by their surface organic (O) horizon that are the major source of DOM to mineral soils, groundwater and headwaters. Boreal forests develop particularly thick moss- covered O horizons often referred to as *mor* (Figure 1.1). With an increased understanding of the catchment scale processes that contribute to stream hydrology and biogeochemistry, the need to understand the contribution of surface O horizons to head-

Figure 1.1: Picture of the hummo-ferric podzol in the Pynn's Brook Experimental Watershed Area (PBEWA) boreal forest and a close up of the detached organic horizon with live vegetation intact.

waters has become increasingly clear (McDowell and Likens, 1988; Boyer et al., 1996; Mcglynn and McDonnell, 2003; Tetzlaff et al., 2014). Three prominent review papers on dissolved organic matter concentrations and fluxes from O horizons were published in the early 2000s (Kalbitz et al., 2001, Michalzik et al., 2001, Neff and Asner, 2001). These reviews highlighted: 1) the importance of hydrology in the mobilization of soil DOM and a need to better understand the nature of the water-DOM flux relationship, 2) the discrepancies that exist between field and laboratory studies likely due to the influence of hydrology in the field that are not captured in the laboratory, and 3) the importance of scale where dominant drivers at small temporal and spatial scales were not relevant at larger scales. Additionally, due to the destructive nature of the lysimeter instrumentation, modelling of the water balance became the preferred method of estimating the water fluxes needed to calculate DOM fluxes. However, these models are often based on assumptions of mineral soil characteristics (i.e., sand, soil, clay content) and do not incorporate macro- and micro-pore flow dynamics (Beven and Germann, 1982; 2013) important to describing the hydrologic behaviour of porous organic horizons, especially those of the moss-covered

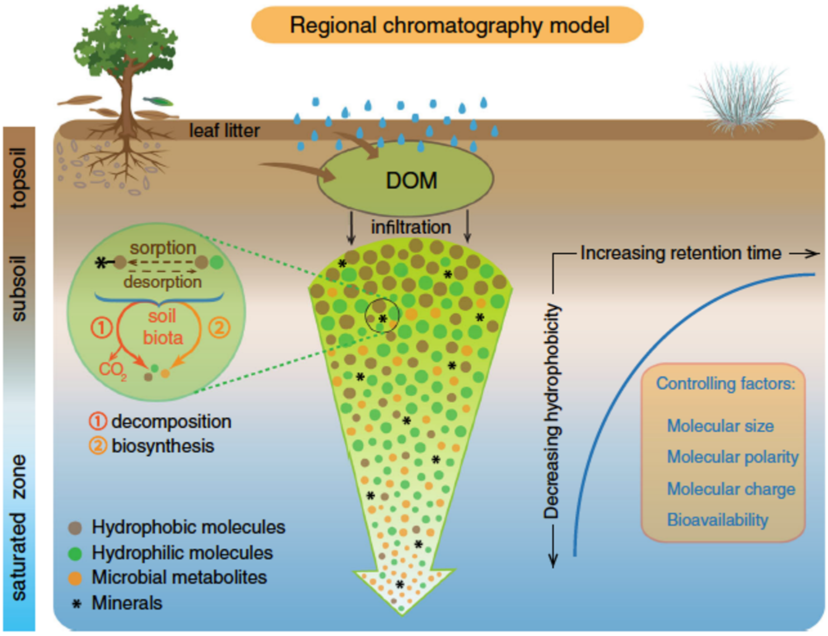

Figure 1.2: Regional chromatography model (Figure 8 from Shen et al., 2015)

boreal forest floor. This presents a limit on our ability to understand the relationship between water and DOM mobilization from organic horizons, and predict future changes to soil organic matter and the linkage between terrestrial and aquatic systems.

The conceptual regional chromatography model of vertical DOM flow through mineral soil demonstrates the driving effect of the chemical character of mobilized DOM on the sequestration potential of minerals soils (Figure 1.2; Kaiser and Kalbitz, 2012; Shen et al., 2015). In general, highly aromatic and hydrophobic materials are more strongly adsorbed by mineral soil and sequestered in the landscape, whereas smaller, hydrophilic materials are more mobile and tend to enter groundwaters and surface waters. In a temperate forest study, the composition of DOM mobilized from O horizons was seasonally variable, with winter and spring dominated by hydrophillic fractions and summer and autumn dominated by hydrophobic fractions in both spruce and beech stands (Kaiser et al., 2001). This suggests that the potential for mineral adsorption vs. export of DOM is seasonally variable. Furthermore, the adsorption capacity of mineral soil is dependent on the direction and rate of water flow paths. Lateral flow within O horizons and along the O - mineral horizon interface occurs in sloped catchments because of the difference in hydraulic conductivity of the two soil horizons. This can result in pipe throughflow that limits delivery to mineral soils but increases direct delivery from surface soil to aquatic systems (Roberge and Plamondon, 1987): a mechanism of DOM export that is of particular importance during storm events (Raymond and Saiers, 2010). Rapid water flow through the catchment during the wet autumn and snowmelt periods limits the residence time of DOM in mineral soils, decreasing the interaction and likelihood of adsorption during two important periods of mobilization and connection to headwaters (Creed et al., 2015). An updated version of the regional chromatography model would take into account the effect of lateral flow and water residence time on the capacity of mineral soils to sequester DOM mobilized from O horizons (for example, see *Figure 1 of* Tank et al., 2018). How DOM composition and water flow paths vary through time and space and interact with each to control the fate of soil DOM requires continued investigation.

1.2 Overview of thesis

In this thesis, I investigated the mobilization of DOM using established boreal forest experimental field sites that address both harvesting and climate change impacts within black spruce and balsam fir boreal forests of eastern Canada. A wide range in climate and topographical conditions exist across Canada's boreal zone. For instance, mean annual precipitation (MAP) ranges from 200 mm to $>$900 mm and PET ranges from 300 mm to $>$550 mm; the balance between MAP and PET means that regions can be separated into discharge-dominated or evapotranspiration-dominated (Krezek et al., 2008). The topography of the eastern boreal zone is such that near surface water flow predominates while the topography of the western boreal is such that vertical and deep subsurface water flow predominates (Figure 1.3; Webster et al., 2015).

Lastly, high seasonality and snow-cover are especially important attributes of boreal forest biogeochemistry and hydrology; two features that are more pronounced in boreal compared to temperate forests. At least half of the precipitation is received as snow in

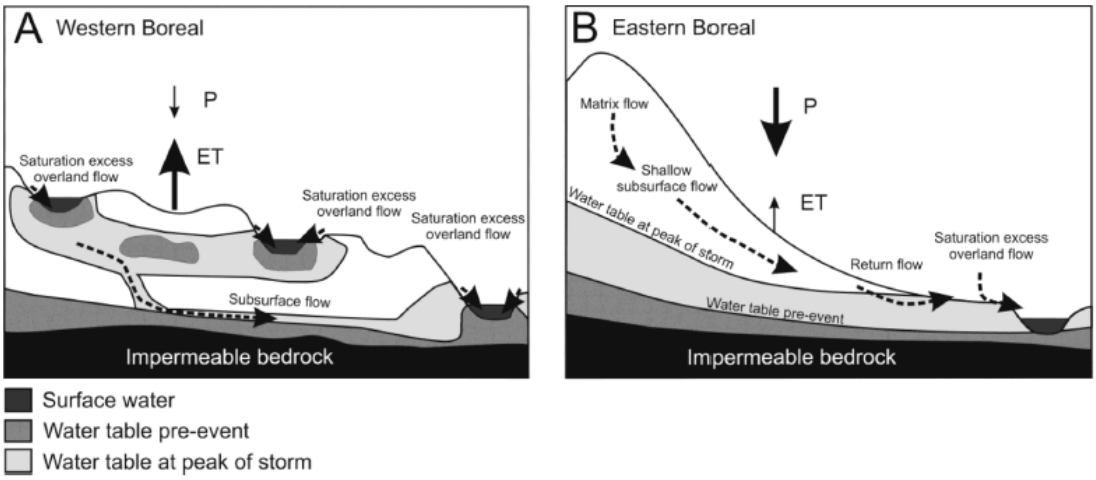

Figure 1.3: Dominant hydrologic flows in (A) western and (B) eastern boreal zones of Canada (Figure 5 in Webster et al., 2015)

much of the boreal zone, and the landscape can be snow-covered for a significant portion of the year. All sites used in this thesis are located within boreal forests of Newfoundland and Labrador and exist within the wet (MAP$>$1000 mm yr^{-1}) maritime boreal climate zone that is discharge-dominated (PET$<$800 mm yr^{-1}).

The Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect (NLBELT) consists of four balsam fir (*Abies balsamea*) dominated forest regions spanning 5° latitude. Mean annual temperature ranges from 0 to 5°C and mean annual precipitation ranges from 1000 to 1500 mm. The NLBELT project uses a space-for-time substitution natural gradient approach where the latitudinal span is representative of an approximate 100-year change in MAT in the boreal zone. These sites have been previously used to investigate the effects of climate on forest ecosystem carbon cycling and stocks (Ziegler et al., 2017), soil N cycling (Philben et al., 2016, 2018), the temperature sensitivity of soil respiration (Laganière et al., 2015; Prodrebarac et al., 2016), and the contributions from microbial communities on soil organic matter cycling (Kohl et al., 2015, 2018). I use these sites in chapter 4 to investigate the relative importance of short-term hydrometeorological variability and long-term climate controls on DOM mobilization from soil organic horizons.

The Pynn's Brook Experimental Watershed Area (PBEWA) was established to address both effects of forest harvesting as well as a hillslope mobilization patterns. It is dominated by black spruce trees (*Picea mariana*) and was clear-cut harvested 10 years prior to this study. Lysimeters were specifically designed to enable year-round sampling with minimal disturbance to the sampling area, and, in order to reduce potential evaporative losses after collection, the lysimeters were connected to a reservoir that collected the sample immediately during collection. In Chapters 2 and 3 of this thesis, the PBEWA was used to understand the effects of harvesting and short-term environmental variability on DOM fluxes, with emphasis on frequent sampling in comparison to what was possible across the remote NLBELT sites. The mobilization of DOM from soil organic horizons was investigated using the passive pan lysimeter method in both NLBELT and PBEWA. Complementary use of the two study areas enabled investigation of DOM mobilization dynamics using the passive lysimeter method at different temporal and spatial scales within the eastern maritime boreal forest zone.

Chapter 2: Is the water-DOC flux relationship seasonally variable? How does harvesting affect this relationship?

Chapter 2 was conducted in the Pynn's Brook Experimental Watershed site to understand the effects of forest harvesting on dissolved organic C (DOC) fluxes, and the short-term relationships between soil moisture, soil temperature, water and DOC mobilization from boreal forest O horizons. Emphasis was placed on frequent sampling in order to capture event- to seasonal-scale variations in the relationship between DOC flux and water fluxes. Lysimeters were designed and constructed at the beginning of this project and used in both this chapter and the following. Special attention was given to winter sampling and the design of a collection reservoir approximately 2 m from the catcher to prevent disturbance of the snowpack during sampling.

Chapter 3: How does the composition of DOM vary seasonally? Is the effect of season altered by forest harvesting?

This chapter was also conducted in the PBEWA and complements Chapter 2 results with detailed compositional information of the DOM fluxes captured by lysimeters in forested and harvested sites. This chapter use optical parameters, such as SUVA and spectral slopes, with DOC:DON and DOC:Fe to understand how the composition of DOM varies on a seasonal basis and how seasonal variation is affected by forest harvesting. This chapter discusses the implications of these compositional variations on the fate of DOM.

Chapter 4: What are the direct and indirect effects of precipitation and temperature on DOM mobilization?

This chapter was conducted in the Newfoundland and Labrador Boreal Ecosystem Transect sites. Four years of passive pan lysimeter collections from three boreal forest regions of the NLBELT (Eagle River, Salmon River and Grand Codroy) enabled an investigation of interannual precipitation and temperature effects on DOM fluxes compared to climate effects as represented by the three regions. To further understand the effects of temperature and precipitation more specific hydrometerological effects were examined. The hydrometeorological factors were selected because they captured either specific features of precipitation (i.e., annual snowfall), temperature (i.e., growing degree days), or the interaction of the two factors (i.e., snowpack duration).

These chapters are written as three separate manuscripts intended for publication as journal articles. Therefore, each chapter contains an abstract, introduction, site description, methods, results, discussion, and conclusions specific to the topic of that chapter. Chapter 2 was published as a journal article in European Geosciences Union (EGU) *Biogeosciences* as Bowering et al., 2020.

Chapter 2

Dissolved organic carbon mobilized from organic horizons of mature and harvested black spruce plots in a mesic boreal region

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Author contributions: KAE and SEZ designed the study with input from KB. KB and KAE designed the lysimeters and planned their installation as well as installation of all environmental monitoring equipment. KB collected and analysed the lysimeter, environmental monitoring and soil properties data. XZ contributed the soil respiration data and analysis. KP contributed soil hydrology data and intrepretations. KB prepared the paper, with editing from SEZ and KAE and further contributions on final drafts from XZ and KP.

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Abstract

Boreal forests are subject to a wide range of temporally and spatially variable environmental conditions driven by season, climate and disturbances such as forest harvesting and climate change. We captured dissolved organic carbon (DOC) from surface organic (O) horizons in a boreal forest hillslope using passive pan lysimeters in order to identify controls and hot moments of DOC mobilization from this key C source. We specifically addressed (1) how DOC fluxes from O horizons vary on a weekly to seasonal basis in forest and paired harvested plots, and (2) how soil temperature, soil moisture and water input relate to DOC flux trends in these plots over time. The total annual DOC flux from O horizons contain contributions from both vertical and lateral flow and was 30 percent greater in the harvested plots than in the forest plots (54 g C m^{-2} vs 38 g C m^{-2} respectively; $p=0.008$). This was despite smaller aboveground C inputs and smaller SOC stocks in the harvested plots, but analogous to larger annual O horizon water fluxes measured in the harvested plots. Water input, measured as rain, throughfall and/or snowmelt depending on season and plot type, was positively correlated to variations in O horizon water fluxes and DOC fluxes within the study year. Soil temperature was positively correlated to temporal variations of DOC concentration ([DOC]) of soil water and negatively correlated with water fluxes, but no relationship existed between soil temperature and DOC fluxes at the weekly to monthly scale. The relationship between water input to soil and DOC fluxes was seasonally dependent in both plot types. In summer, a water limitation on DOC flux existed where weekly periods of no flux alternated with periods of large fluxes at high DOC concentrations. This suggests that DOC fluxes were water limited and that increased water fluxes over this period result in proportional increases in DOC fluxes. In contrast, a flushing of DOC from O horizons (observed as decreasing DOC concentrations) occurred during increasing water input and decreasing soil temperature in autumn, prior to snowpack development. Soils of both plot types remained snow-covered all winter, which protected soils from frost and limited percolation. The largest water input and soil water fluxes occurred during spring snowmelt, but did not result in the largest fluxes

of DOC, suggesting a production limitation on DOC fluxes over both the wet autumn and snowmelt periods. While future increases in annual precipitation could lead to increased DOC fluxes, the magnitude of this response will be dependent on the type and intra-annual distribution of this increased precipitation.

2.1 Introduction

Boreal forests occupy 11 percent of the total land surface and thus span a variety of topographies and climate zones (Bonan and Shugart, 1989). They contain organic matter rich soils that store approximately 19 percent of the global soil organic carbon (SOC) pool (Pan et al., 2011). Losses of SOC from land occurs predominately through decomposition and mobilization as CO_2 to the atmosphere. A secondary loss pathway of SOC occurs through solubilization and mobilization as dissolved organic carbon (DOC) to deeper SOC pools, groundwater and surface waters. While losses of SOC as CO_2 to the atmosphere, representing approximately 40 percent of boreal forest GPP (Luyssaert et al., 2007), are accounted for, losses of SOC as DOC to surface waters are often not included in carbon budget models. This is despite the potential for DOC losses to offset ecosystem carbon sink estimates (Gielen et al., 2011: Webb et al., 2019). A mechanistic understanding of the role of DOC at the ecosystem scale is necessary for accurate accounting of the net ecosystem carbon balance (NECB) and for predicting how ecosystems will function under changing environmental conditions (Chapin et al., 2006; Marin-Spiotta et al., 2014).

The importance of upland forest SOC as a source of DOC to boreal forest surface waters is variable among boreal regions due to differences in connectivity driven by topography and precipitation (McGlynn and McDonnell, 2003). In low relief catchments, SOC mobilized as DOC from upland forest soil may be lost as CO_2 or sequestered within deeper mineral soil pools rather than reaching surface waters. The SOC of the riparian zone represents an important DOC source to streams in these areas (Ledesma et al., 2017).

High relief catchments, however, are examples where upland forest soils can be much more connected to surface waters, especially during large precipitation events (Raymond and Saiers, 2010) and periods of the year when the water table is high (Laudon et al., 2011; Schelker et al., 2013). Therefore, the importance of the upland forest SOC contribution to surface waters is not generalizable across boreal forest ecosystems, constituting examination within specific regions and under different environmental conditions.

The upper organic (O) horizons of podzols are key sources of soil DOC (Mcdowell and Wood, 1985). The large range in values of O horizon DOC fluxes reported from field studies in temperate and boreal forest systems (3–122 g C m^{-2} at 5 cm depth, Neff and Asner, 2001; 10–40 g m^{-2} y^{-1}, Michalzik et al., 2001) are due to both real variability, and variability associated with the usage of different methodologies. Real-world variability is expected given the known spatial heterogeneity of soil and hydrological aspects of forests (Creed et al., 2002). Hydrology was long ago thought to be more important than biological controls, although clarification of the water flux-DOC flux relationship was suggested as an area of further research (Kalbitz et al., 2000; Neff and Asner, 2001). More recent field studies therefore focused on specific hydrological controls, such as annual throughfall inputs (Klotzbücher et al., 2014), soil drying followed by rewetting (De Troyer et al., 2014), soil frost (Haei et al., 2010), and snowmelt (Finlay et al., 2006). However, climate transect studies within the boreal forest zone revealed greater DOC fluxes at warmer (low-latitude) relative to cooler (high-latitude) sites, suggesting that this difference can be explained by higher N deposition (Kleja et al., 2008) or higher net primary productivity (Fröberg et al., 2006; Ziegler et al., 2017) in the lower latitude sites. The DOC fluxes from O to mineral horizons in white pine stands was observed to be negatively correlated with stand age, (Peichl et al., 2007), and a stand species comparison study demonstrated larger DOC fluxes from the thicker O horizons of Norway spruce (*Picea abies*) stands relative to silver birch stands (*Betula pendula*; Fröberg et al., 2011). It is likely that a combination of hydrological and biogeochemical factors regulate DOC production and mobilization through soil, but the relative importance of each of these factors is dependent on the scale of investigation, both spatially and temporally (Michalzik et al., 2001), and remains to be confirmed. Black spruce (*Picea mariana*) dominate North American boreal forests (van Cleve et al., 1983; Bona et al., 2016) and these forests span a wide range of environmental conditions that drive variations in SOC decomposition (Wickland et al., 2007) and SOC persistence across sites (Schmidt et al., 2011). Forest harvesting increases water yield (Neary, 2016) and reduces C in the organic layers due to reductions in litter fall and increases in soil respiration (James and Harrison; 2016), but the extent of the impact on soil properties and biogeochemical cycling is dependent on many interacting site specific variables (Kreutzweiser et al., 2008). Furthermore, while lysimeter studies conducted in post-harvested forests found immediate increases in DOC fluxes from O horizons (Kalbitz et al., 2004; Piirainen et al., 2002), the longer term effects of harvesting on DOC mobilization have not been considered. We exploited spatially (plot type) and temporally (weekly to seasonal) variable environmental conditions in a maritime boreal black spruce hillslope site to investigate the processes controlling DOC fluxes from O horizons. The region receives moderately high annual precipitation (1200 mm yr^{-1}) and is snow-covered for approximately 1/3rd of the year. The objectives of this study were: 1) to measure DOC fluxes over one year from O horizons of podzols in two contrasting boreal plots that are typical of the managed boreal forest 2) to measure short term variations of DOC fluxes across seasons in order to understand how environmental conditions vary in relation to DOC fluxes. These results will faciliate a process based understanding of DOC mobilization from O horizons which is important to describing site specific terrestrial to aquatic C linkages and refining forest C budget models.

2.2 Materials and Methods

2.2.1 Site Description

This study was conducted in an experimental harvest site within a mature black spruce forest at the Pynn's Brook Experimental Watershed Area (PBEWA) located 50 km from Deer Lake, western Newfoundland and Labrador, Canada. (48° 53'14" N, 63° 24' 8" W). The site consists of 2 hectares divided into eight 50 x 50 m plots (note: only six were used in this study; Figure 2.1A). Four of the plots were left un-harvested and four were randomly selected for clear-cutting. The four clear-cut plots were harvested on July 07-10, 2003 using a short-wood mechanical harvester, with minimal disturbance to the underlying soil and with any deciduous trees left standing. Further information on site preparation and conditions can be found in Moroni et al., 2009. The harvested plots were not replanted following clear-cutting and had naturally recovered moss, herb and shrubbery by the time of sampling for this study, but the regeneration of conifers remains scarce. The 10-year post harvest plots will be referred to as harvested plots and the mature 80-year-old black spruce plots will be referred to as forest plots throughout. Soils are classified as humo-ferric podzols with morainal parent material (Moroni et al., 2009).

2.2.2 Lysimeter Installation and Sample Collection

Passive pan lysimeters were installed at the interface between the O and mineral horizon. Each lysimeter footprint was 0.3 m by 0.4 m and collected water percolating through the O horizon, including both vertical and lateral flow (Figure 2.1B,C), with a maximum solution collection capacity of 25 L. The lysimeters were designed using reported recommendations for achieving accurate volumetric measurements of soil leachate (Radulovich and Sollins, 1987; Titus et al., 1999). It was desirable for this study that: 1) the collection pan directs leachate immediately into a deeper storage container, avoiding potential issues of sample evaporation from the collection pan, and 2) the buried storage reservoir

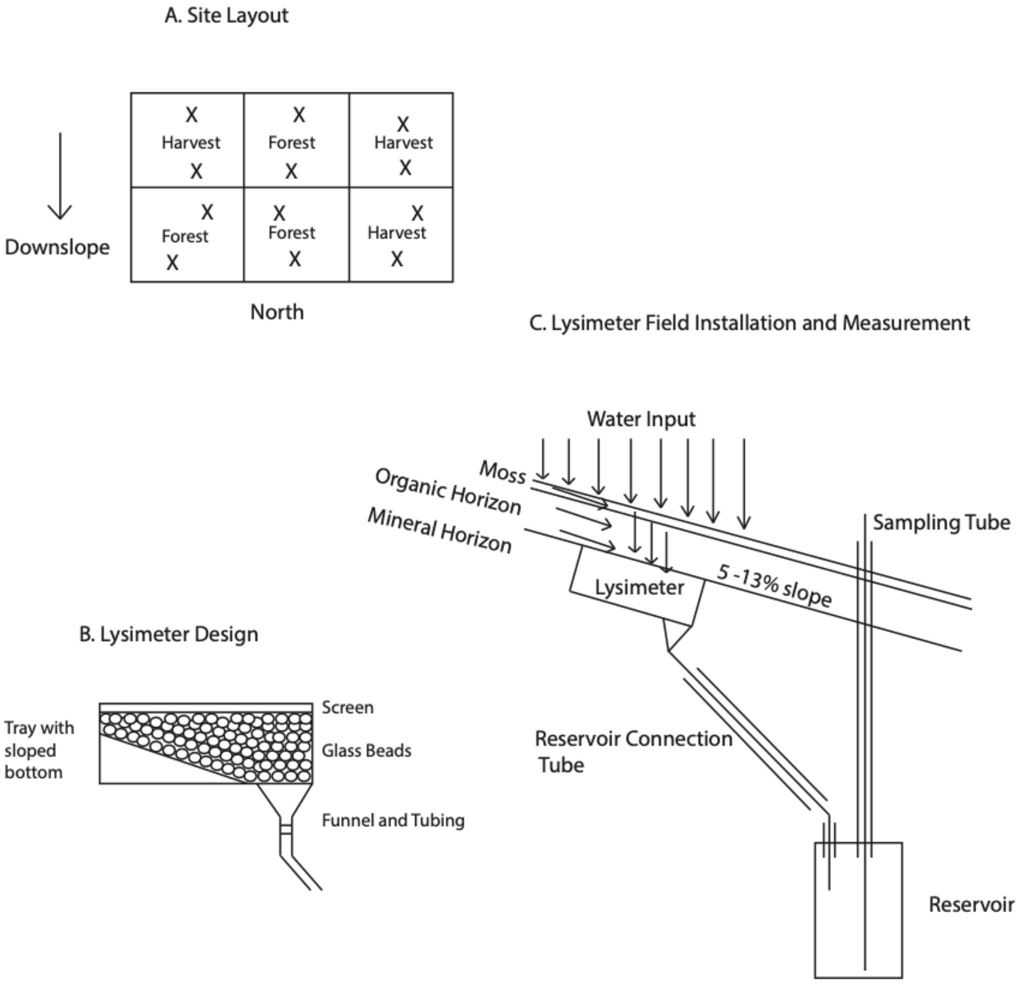


Figure 2.1: Pynn's Brook Experimental Forest Design. A north facing black spruce hillslop site divided into six 50 x 50 m plots, half of which were randomly selected for harvest 10 years prior to lysimeter installation (A). Each plot contains two lysimeter pairs ("X") for a total of 12 harvest and 12 forest lysimeters. The lysimeters consisted of a HDPE tray with a sloped bottom connected to a funnel and PEX tubing (B). Each lysimeter was installed between the moss + organic and the mineral horizons on a slope ranging between 5 -13%. Water collected by the lysimeters infilitrated vertically and laterally through moss and organic layers and into a 25 L reservoir from which samples were retrieved (C)

was placed away from the collection pan so that soil and snowpack directly above and upslope from collection area was not disturbed during sample collection.

Installation of lysimeters began in July 2012 and was completed the following spring in May 2013. Four lysimeters were installed in three plots of each plot type for a total of 12 forest lysimeters and 12 harvested lysimeters. The slope measured at each lysimeter was 5 - 12% and 7 – 13% in the forest and harvested plots, respectively. Collection began on July 12, 2013 from forest and harvested lysimeters. Synchronized sampling from lysimeters of both plot types was carried out every 7 to 15 days from July to January, once between January and April, and every 7 to 15 days from April to July. Lysimeter samples were stored at 4°C immediately following collection, were filtered using pre-combusted GF/F-size Whatman filter paper, preserved with mercuric chloride within 24 hours of collection, and stored at 4°C in the dark until analysis. The DOC concentration of each lysimeter sample was measured using a high-temperature combustion analyzer (Shimadzu TOC-V). The measured DOC concentration, the total volume collected by lysimeters, the number of collection days, and the lysimeter collection area were used to calculate a DOC flux (g C m^{-2} d^{-1}). Water flux was calculated using the measured lysimeter volume on each collection day and the lysimeter collection area (L m^{-2} d^{-1}).

Lysimeter collection efficiency testing was completed on 3 forest lysimeters and 3 harvested lysimeters following the study period. The soil on top of and around the lysimeter catchment area was first saturated, and then the area directly above each lysimeter was watered uniformly with 10 L of water and the volume of solution collected by the lysimeters was retrieved. This was repeated 3 times on each of the lysimeters to determine the efficiency of the lysimeter system in collecting the leachate from the footprint of organic soil directly above the installed pan. Lysimeter efficiency was found to be 92.3 ± 21% and 88.6 ± 18% in the forest and harvested plots, respectively. No statistically significant difference between the collection behavior of the forest and harvested forest plot lysimeters was detected (t-test; p=0.8248).

2.2.3 Water Input Estimate

A tipping bucket rain gauge (RST Instruments Model TR-525) was installed in an open area at PBEWA to monitor local precipitation and air temperature. Data from the local tipping bucket were compared with regional precipitation reported by Environment Canada at the Deer Lake Airport (49° 13’ 00” N, 57° 24’ 00” W) approximately 50 km away. Total precipitation measured at the Deer Lake Airport was found to be a good predictor of PBEWA precipitation on weekly timescales for the dates available ($n = 30$, $y = 0.96x + 2.35$, $r^2 = 0.9145$, $p < 0.0001$). This relationship was used to calculate weekly precipitation for a gap in our onsite precipitation data between July 24 and August 29, 2013. The onsite gauge was not outfitted to partition total precipitation into snowfall and rainfall and therefore snowfall was calculated by applying the proportion of rain and snow measured at the Deer Lake Airport station to the total precipitation measured at PBEWA.

Snowmelt water input was estimated using changes in snow depth between each lysimeter collection day measured near each lysimeter in both the forest and harvested plots. The average snow depth change by plot type was multiplied by an estimated maritime snow density of 0.343 g cm^{-3} (Sturm et al. 2010) to provide an estimated snowmelt water input value. Snow density is variable both within the snow profile and over the course of snowmelt, therefore this calculation provides a rough estimate of the water input to the soil from snowmelt. These estimates were combined with rainfall when applicable to give a total water input over the lysimeter footprint for each collection period.

A snow pit was analyzed for each plot type on April 2, 2014 just prior to the onset of snowmelt. A series of 15 cm long snow cores were collected beginning from the top of the snowpack down to the forest floor to obtain a sample of the entire snowpack per plot type. The cores were melted and pooled by plot type. The DOC content of pooled samples was measured to provide a mean DOC concentration in the snow of forest and harvested plots. The snow depth of each plot, combined with the estimated snow density (0.343 g cm^{-3}) and DOC concentration was used to determine a snow DOC input to the forest floor (Table 2.1).

Throughfall was collected on an event basis using 10 buckets (0.36 m^{-2} collection area) distributed within a 50 x 50 m forest plot in May, August and October 2015. Synchronized collection of open rainfall using 5 buckets was completed in an adjacent harvested plot. Prior to the first sampling date a preliminary variability experiment was conducted in October 2015 onsite to determine the most practical number of buckets required to capture the variability within forest and harvested plots. Forty buckets were installed in a forest plot and ten in a harvested plot and left out for one rain fall event. The contents of each bucket was sampled, filtered and analyzed for DOC concentration. From these data a Monte Carlo simulation was used to predict the relationship between number of buckets deployed and the variability of DOC concentration captured. It was found that installing ten buckets in the forest plots, and five in the harvested plots captured a similar amount of variation in water volume and DOC concentration as deploying forty gauges in the forest plot and ten in the harvested. Mean DOC concentrations of each collection was determined for each collection period and used as a seasonal representation of forest and harvested DOC concentrations. Seasonal DOC was then scaled up to an annual DOC input estimate (Table 2.1).

2.2.4 Soil Sampling

The O horizon soil was sampled specifically for this study by taking three 20 x 20 cm samples from three forest plots and three 20 x 20 cm samples from three harvested plots (n = 9 for each plot type). Living vegetation was removed, the thickness of each sample was measured, and the soil was sieved using a 6 mm sieve and dried at 50°C for 48 hours. Samples were ground using a Wiley mill and subsampled for elemental analysis on a Carlo Erba NA1500 Series II Elemental Analyser (Milan, Italy) at Memorial University of Newfoundland. These samples were used to determine soil % C, soil C stock (kg C m^{-2}). Mineral soil was sampled below each O horizon sample with a soil corer (length: 15 cm, diameter: 5.5 cm). Each mineral soil sample was sieved using a 2 mm sieve and dried at 50°C for 48 hours and weighed. Once dried and weighed, samples were ground

Table 2.1: Ecosystem and soil properties of black spruce forest and adjacent harvested plots. Values are means of 12 litterfall traps per plot type, 16 soil respiration collars per plot type, 3 organic (O) horizon soil temperature and moisture probes per plot type, 2 mineral horizon soil temperature and moisture probes per plot type, 9 O horizon samples per plot type used to determine thickness, %C, C stock, C:N and bulk density, 1 snow pit per plot type, and 3 seasonally distinct rain collections used together with annual rainfall to estimate an annual C input, with standard error in parenthesis. Results for one way ANOVAs (litterfall, O horizon thickness, and soil %C, C stock, C:N, soil bulk density) and T-tests (soil temperature and moisture) conducted to identify plot type differences are shown where applicable with significant results in bold (alpha=0.05). Soil moisture is measured as volumetric water content (VWC). See methods for further measurement and sample collection details.

	Site				
Annual Air Temperature (°C)	4.4				
Annual Precipitation (mm)	1402.4				
Rainfall (mm)	908.4				
Snowfall (cm)	516.2				
	Forest	**Harvested**	**T value**	**F value**	**p value**
Litterfall					
Total mass (g m^{-2} y^{-1})	**240.9** (14.7)	**13.7** (3.2)	-	309.0	**<0.0001**
Total carbon (g C m^{-2} y^{-1})	**130.9** (8.0)	**7.4** (1.7)	-	287.6	**<0.0001**
Rain (g DOC m^{-2} y^{-1})	5.5	3.9	-	-	-
Snow (g DOC m^{-2} y^{-1})	2.1	1.3	-	-	-
Soil Respiration (g C m^{-2} y^{-1})	711.9 (59.5)	672.2 (32.3)	-	0.226	0.651
Organic horizon					
Soil T (°C)	**6.1** (0.03)	**7.1** (0.12)	-11.31	-	**0.003**
Soil M (cm^{3}cm^{-3})	0.34 (0.08)	0.41 (0.11)	-1.289	-	0.386
Thickness (cm)	**8.17** (0.6)	**4.26** (0.6)	-	18.37	**0.013**
% C	47.6 (0.7)	43.0 (2.7)	-	1.07	0.121
C stock (kg C m^{-2})	**2.39** (0.18)	**1.34** (0.26)	-	12.15	**<0.0001**
Bulk density (g cm^{-3})	0.06 (0.007)	0.07 (0.004)	-	3.08	0.154
Mineral horizon (top 15 cm)					
Soil T (°C)	6.2 (0.2)	7.2 (0.1)	NA	NA	NA
Soil M (cm^{3}cm^{-3})	0.40 (0.02)	0.48 (0.03)	NA	NA	NA
% C	2.63 (0.41)	2.17 (0.42)	-	0.996	0.375
C stock (kg C m^{-2})	3.85 (0.79)	5.33 (0.81)	-	3.123	0.152
Bulk density (g cm^{-3})	1.2 (0.6)	1.6 (0.5)	-	0.121	0.746
% rock by volume	84 (3)	64 (7)	-	0.355	0.133

using a ball mill and subsampled for elemental analysis as above for O horizon samples. The % rock fragments ($<$2mm) by volume was estimated using the weight of rocks and Eq. (1):

$$Z2 = Z1\ (2 - Z1)$$

where $Z2$ = % rock by volume, $Z1$ = % rock by weight

(Brakensiek and Rawls, 1994)

Bulk density of O horizon and mineral soils was calculated using the volume and dried mass of the soil sample. Additionally, two sets of O horizon samples were obtained for physical measurement of O horizon unsaturated and saturated hydraulic properties and water infiltration rates. Cores (5 cm diameter) were collected in triplicate at two locations in forest and harvested plots (6 cores per plot type) and live moss was removed prior to analysis using a HYPROP system. The HYPROP measurements of water content and soil water tension during continuous evaporation were analysed to obtain relationships of soil water tension and hydraulic conductivity to water content (Schindler and Muller, 2006; Schindler, 2010). A second set of cores (10 cm diameter) were collected at six locations in two forest plots for falling head infiltration (INF) analysis. These cores included the entire organic (L,F, and H) horizon and moss. Following a first round of infiltration rate measures a subset of cores were partially excruded to expose the entire H horizon, which was carefully removed before remeasuring infiltration. Forest and harvested plots had H layers with similar bulk densities, but H layers constituted much of the O horizon in harvested plots where moss cover was limited and the L and F layers were reduced in comparison to forest plots. Matrix and macropore saturation was determined for each these cores (Table 2.4).

2.2.5 Litterfall Collection

Litterfall was collected using four 0.34 m^2 litter traps placed on the forest floor in four plots per plot type from August 2012 to August 2013. Litter was collected in early spring and late fall, sorted into needles, bark, cones, lichen and deciduous leaves, dried at 60 °C over 48 hours, and weighed. A litterfall C input was estimated by applying concentrations of 542 mg C g^{-1} for both twigs and needles and 552 mg C g^{-1} for cones of black spruce litter fall (Preston et al., 2006).

2.2.6 Soil Temperature and Moisture

Three soil temperature and moisture probes per plot type (Decagon ECH2O -TM) were installed mid- organic horizon at approximately 5-cm depth, and two were installed in the mineral layer at approximately 15-cm depth. These probes measure the dielectric constant of the soil using capacitance/frequency domain technology, providing volumetric water content (VWC). The O horizon probes were calibrated using HYPROP and infiltration analyses (Table S7; see also “Methods: Soil Sampling” and Table 2.4). Handheld spot measurements using a HydroSense II Soil Water Content Reflectometer on select days (data not shown), confirmed the consistently wetter O horizons in the harvested plots as indicated by field probe measurements (Figure 2.2C; Table 2.1).

2.2.7 Soil Respiration

Measurements of soil respiration were made at biweekly intervals for the snow-free growing seasons (May–November) in 2013-2015. Four collars consisting of a 7-cm section of 10-cm inside diameter PVC pipe were inserted into the ground 8 months prior to the start of measurement in four forest plots and four harvested plots. Soil respiration rate and soil temperature were measured every two weeks using a LI-6400-09 soil chamber and a penetration soil temperature probe, both attached to LI-6400 portable CO_2 infrared gas analyzer (IRGA). Volumetric soil water content was measured with a Campbell HydroSense penetration probe inserted in the soil to the depth of 10 cm in the vicinity of the PVC collars. Daily soil respiration rates were modelled using daily average air temperature and the relationship between measured instantaneous soil respiration and temperature. Annual cumulative growing season soil respiration was calculated using the annual sum of modelled daily soil respiration.

2.2.8 Statistical Analyses

All statistical analyses were performed using RStudio version 1.0.136. T-tests were used to determine plot type differences in mean annual soil moisture and soil temperature. ANOVAs were used to determine plot treatment differences in total annual DOC flux, water flux and DOC concentration, mean organic horizon thickness, mean organic and mineral soil % C, mean organic and mineral soil C stocks, and mean annual litterfall between forest plots and harvested plots over the entire study period (Table 2.1, Table S1, Figure 2.2; asterisks). A repeated measures linear mixed effects (RM-LME) model using the ‘nlme’ package (Pinherio et al., 2020) was used to assess the fixed effects of collection day, and the interaction between collection day and plot type on the intra-annual variation of DOC fluxes, water fluxes, and DOC concentration (Table S2) with lysimeter as the random effect. Post-hoc Tukey tests were used to determine significant differences in DOC flux, water flux and DOC concentration between forest and harvested forest plots on individual collection days (Figure 2.2D-E; asterisks). The data were grouped into three seasons: summer, autumn and spring snowmelt, and a two way ANOVA was used to assess the effects of water input, season and their interaction on DOC fluxes (Table 2.3).

Correlation testing was used to assess the relationships among data from lysimeter collections (DOC flux, water flux and DOC concentration) and mean soil temperature, mean soil moisture and daily water input (Table 2.2) across 30 collection days. Multiple regressions were not used due to the multi-collinearity of many of the predictor variables, which affected the estimated regression parameters. Individual correlations, however, were assessed to evaluate the strength of relationships among variables within the dataset.

A linear mixed effects model was used to examine the effects of plot type, sample year (2013–2015), and their interactions on soil respiration. The interaction term was further analysed with a post-hoc least square means test. Linear interpolation was used to calculate cumulative soil respiration for the snow-free growing season during the period of 2013–2015. A multiple linear regression was used to explain the dependence of soil respiration on soil temperature, moisture and the soil temperature by soil moisture interaction.

2.3 Results

2.3.1 Soil Properties and Aboveground Litterfall

Soil bulk density was not different between the forest and harvested plots for either O or mineral soil horizons (Table 2.1). However, O horizon depth was almost twice as great in the forest plots compared with the harvested plots (means of 8.17 cm and 4.26 cm respectively; Table 2.1). This resulted in an estimated 78% greater O horizon SOC stock in forest plots relative to harvested plots (2390 g C m^{-2} and 1340 g C m^{-2}; Table 2.1). Annual litterfall inputs to the soil surface were greater in the forest plots (240.9 g m^{-2} y^{-1} and 13.7 g m^{-2} y^{-1}), amounting to an estimated 130.9.4 g C m^{-2} y^{-1} and 7.4 g C m^{-2} y^{-1} reaching the forest floor as litterfall in the forest and harvested plots respectively (Table 2.1).

2.3.2 Soil Respiration

The temporal range in instantaneous CO_2 efflux rates during the lysimeter measurement period (July 2013 – July 2014; Figure 2.2A) was approximately 2.0 – 4.8 g C m^{-2} d^{-1} in the forest and harvested plots. The estimated cumulative respiration was 672.2 and 711.9 g C m^{-2} y^{-1} in the forest and harvested plots, respectively. Highest efflux rates occurred in the summer and decreased to lowest values in autumn in both plot types. Lowest rates occurred following snowmelt and increased in both plot types as soils warmed.

There was no overall significant difference in soil respiration between plot types for the 2013- 2015 growing season estimates however, there was a significant plot type by sample year interaction effect on soil respiration (Table S3). The multiple comparisons found that soil respiration in the harvested plot was lower relative to that in the forest plot for 2014 and 2015 growing seasons, but not 2013 (Table S4 and S5). Soil respiration was positively related with soil temperature but negatively related with soil moisture content, and the presence of a soil temperature by soil moisture interaction on soil respiration in the regression analysis indicated the effects of soil temperature on soil respiration had been modified by soil moisture (Table S6).

2.3.3 Environmental Conditions

The local mean annual air temperature over the July 2013 to July 2014 study period was + 4.4°C (daily mean range: - 19.0°C to + 25.9°C), and 1402.4 mm of total precipitation fell, including 516 mm water equivalents as snowfall. The greatest total precipitation occurred over the winter period (600.2 mm), followed by the summer (388.2 mm), autumn (332.1 mm) and then snowmelt (81.9 mm). Two significant dry spells were observed in summer (10 consecutive days of $<$10mm day^{-1} of rainfall, Figure 2.2; shaded areas). The greatest total snow fall occurred during the winter period (481.9 cm). Total autumn snowfall was 18.6 cm, and snowmelt snowfall was 15.8 cm, and no snow fell in the summer. The snowpack depth measured at the onset of snowmelt on April 2nd 2014 was 83 cm in the forest plots and 110 cm in the harvested plots.

The O horizons in the harvested plots were generally warmer and thinner than those in the forest plots (Table 2.1, Figure 2.2; forest plot range: 1.1°C to 16°C; harvested plot range: 1.4°C to 20°C). In summer, soil temperatures maintained an approximate 2°C difference. Decreasing air temperature in the autumn was associated with a convergence of soil temperature such that winter soil temperatures in the two different plot types were similar. Increasing air temperatures in the spring and snowmelt resulted in a divergence of soil temperature in the two plot types (Figure 2.2B). The snowpack persisted throughout

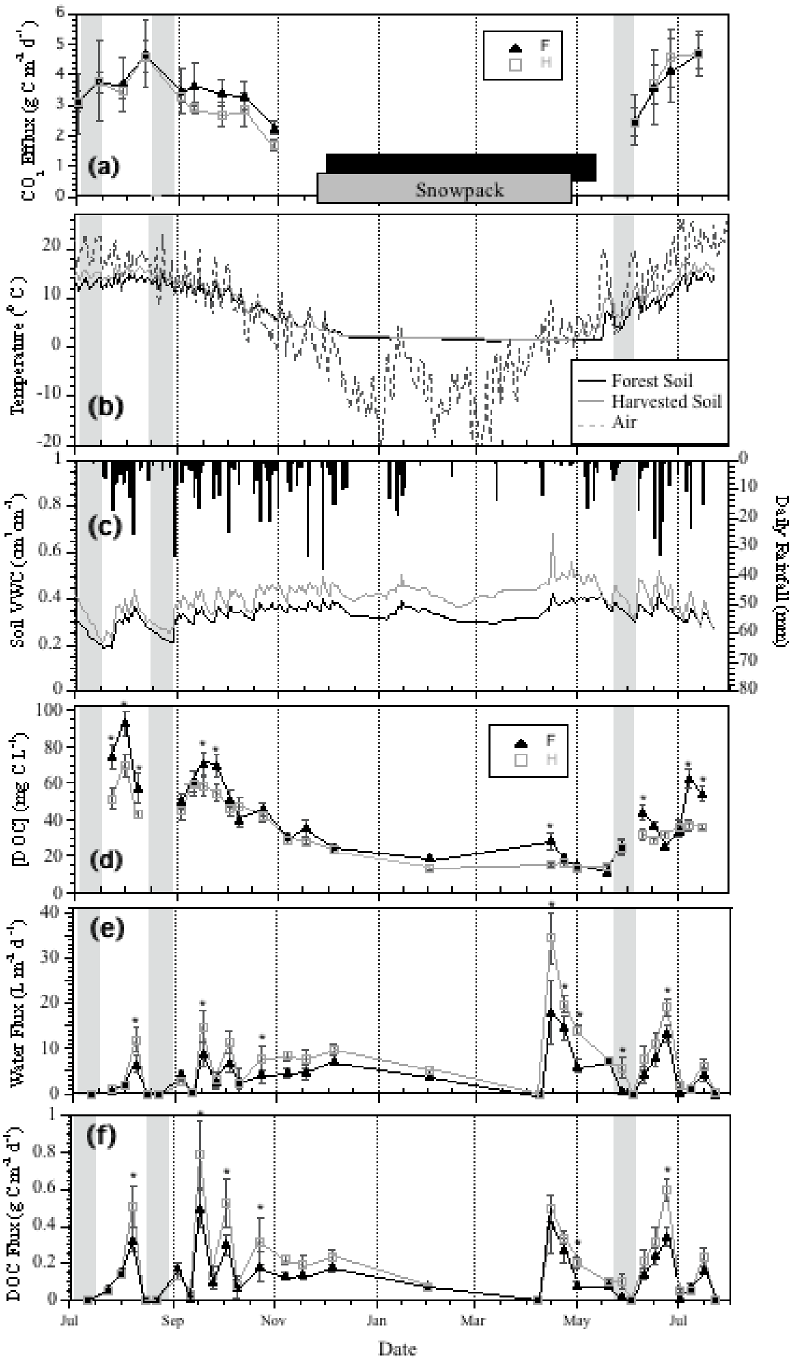


Figure 2.2: Temporal variation of environmental and lysimeter-captured variables. Soil respiration (a), daily mean soil temperature with the presence of a snowpack indicated by the grey (harvested) and black (forest) bar (b), daily rainfall and daily mean soil moisture (c), and lysimeter collections (d,e,f) from July 2013 to July 2014 in black spruce forest and harvested plots. The mean dissolved organic carbon (DOC) concentration (d), water flux (e), and DOC flux (f) was determined using passive pan lysimeter collections underneath O horizons. Lysimeter sampling was continuous and points represent a mean daily flux over each collection period. Error bars show standard error of the mean of 12 lysimeter collections per plot type per collection period. Grey shading areas indicate dry periods signified by those exceeding 10 consecutive days of rainfall less than 10mm/day, corresponding to periods of soil drying. Significant differences in DOC flux, water flux and DOC concentration between plot type on each collection day where determined by repeated measure linear mixed model post hoc tests and are indicated by an asterisk (alpha = 0.05).

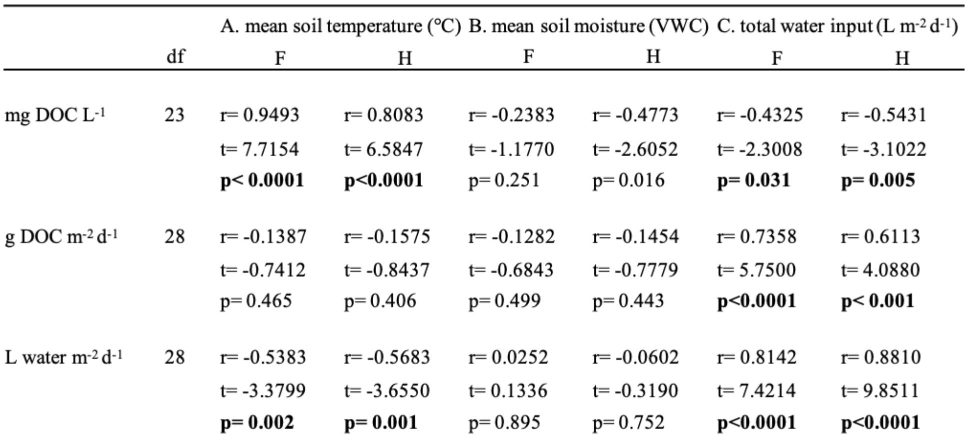
winter and insulated the soils of both plot types from freezing. Soil temperatures began increasing in the spring about two weeks earlier in the harvested plots than in the forest plots, indicating an approximate two- week lag in the snow free period in the forest plots compared to the harvested plots (Figure 2.2A; snowpack).

The O and mineral horizons were consistently wetter in harvested plots relative to the forest plots over the duration of the study (Figure 2.2C), but given the high variability and few measurement replicates (n=3 O horizon, n=2 mineral horizon) this pattern was not statistically confirmed (Table 2.1). The O horizons experienced long periods of drying in the summer, especially in July 2013 (Figure 2.2C; shaded areas) but there was little change in soil moisture over the winter other than during a 2 week episode of warming and snowmelt in January 2014.

2.3.4 DOC Concentration

The mean annual volume weighted DOC concentration collected by lysimeters was 29.4 and 26.1 mg C L^{-1} in the forest and harvested plots (Figure 2.3A) was not statistically different ($p=0.09$). The mean annual DOC concentration was volume weighted because lysimeter collections were not made at even time intervals throughout the year. Seasonal ranges of absolute concentrations include summer mean concentrations of 55 and 45 mg C L^{-1}, autumn means of 42 and 38 mg C L^{-1}, winter means of 18 and 13 mg C L^{-1}, and spring snowmelt means of 25 and 20 mg C L^{-1} in the forest and harvested plots, respectively. The DOC concentration exhibited an interaction of collection day by plot type; higher DOC concentrations were measured in forest plots relative to the harvested plots in 9 of 25 sampling times, most commonly observed during summer and early autumn. No differences in DOC concentration were detected between plot types during the late autumn and winter (October to April; Figure 2.2D). Intra-annual variation in DOC concentration was correlated to soil temperature (positive correlation; Table 2.2) and water flux variation (negative correlation; Table 2.2) in both plot types. The DOC concentration was negatively correlated to soil moisture in the harvested plots only.

Table 2.2: Pearson correlations between lysimeter captured dissolved organic carbon concentrations (mg DOC L^{-1}), dissolved organic carbon fluxes (g DOC m^{-2} d^{-1}), soil solution fluxes (L water m^{-2} d^{-1}) and environmental variables (mean soil temperature, mean soil moisture and daily water input rain and/or snowmelt) over 30 collection periods.



		A. mean soil temperature (°C)		B. mean soil moisture (VWC)		C. total water input (L m^{-2} d^{-1})	
	df	F	H	F	H	F	H
mg DOC L^{-1}	23	r= 0.9493 t= 7.7154 **p< 0.0001**	r= 0.8083 t= 6.5847 **p<0.0001**	r= -0.2383 t= -1.1770 p= 0.251	r= -0.4773 t= -2.6052 p= 0.016	r= -0.4325 t= -2.3008 **p= 0.031**	r= -0.5431 t= -3.1022 **p= 0.005**
g DOC m^{-2} d^{-1}	28	r= -0.1387 t= -0.7412 p= 0.465	r= -0.1575 t= -0.8437 p= 0.406	r= -0.1282 t= -0.6843 p= 0.499	r= -0.1454 t= -0.7779 p= 0.443	r= 0.7358 t= 5.7500 **p<0.0001**	r= 0.6113 t= 4.0880 **p< 0.001**
L water m^{-2} d^{-1}	28	r= -0.5383 t= -3.3799 **p= 0.002**	r= -0.5683 t= -3.6550 **p= 0.001**	r= 0.0252 t= 0.1336 p= 0.895	r= -0.0602 t= -0.3190 p= 0.752	r= 0.8142 t= 7.4214 **p<0.0001**	r= 0.8810 t= 9.8511 **p<0.0001**

The mean DOC concentration in the snowpack, measured immediately prior to snowmelt on April 2 2014, was 7.5 mg C L^{-1} and 3.3 mg C L^{-1} in the forest and harvested plots, respectively. Total snow depth of 84 cm and 110 cm amounted to a potential DOC input to the soil of 2.1 g C m^{-2} and 1.2 g C m^{-2} over the course of snowmelt in the forest and harvested plots, respectively (Table 2.1). The mean DOC concentration in rain throughfall measured in one forest plot was 7 mg DOC L^{-1} and open rainfall measured in one adjacent harvested plots was 3 mg DOC L^{-1}, consistent across May, June and October samples. The estimated annual rain DOC input to soil was 5.5 g m^{-2} and 3.9 g m^{-2} in the forest and harvested plots, respectively (Table 2.1).

2.3.5 Lysimeter captured water and DOC Fluxes

The mean annual O horizon water flux was 2040 L m^{-2} (+/- 129) in the harvested plots and 1366 L m^{-2} (+/- 344) in forest plots, revealing a 49% greater flux of water through the O horizons in the harvested plots relative to the forest plots (Figure 2.3B; p= 0.0357). This corresponded to DOC fluxes of 54 g C m^{-2} (+/- 3) and 38 g C m^{-2} (+/- 5) in the harvested and forest plots, respectively, representing a 30% greater annual loss of DOC from the

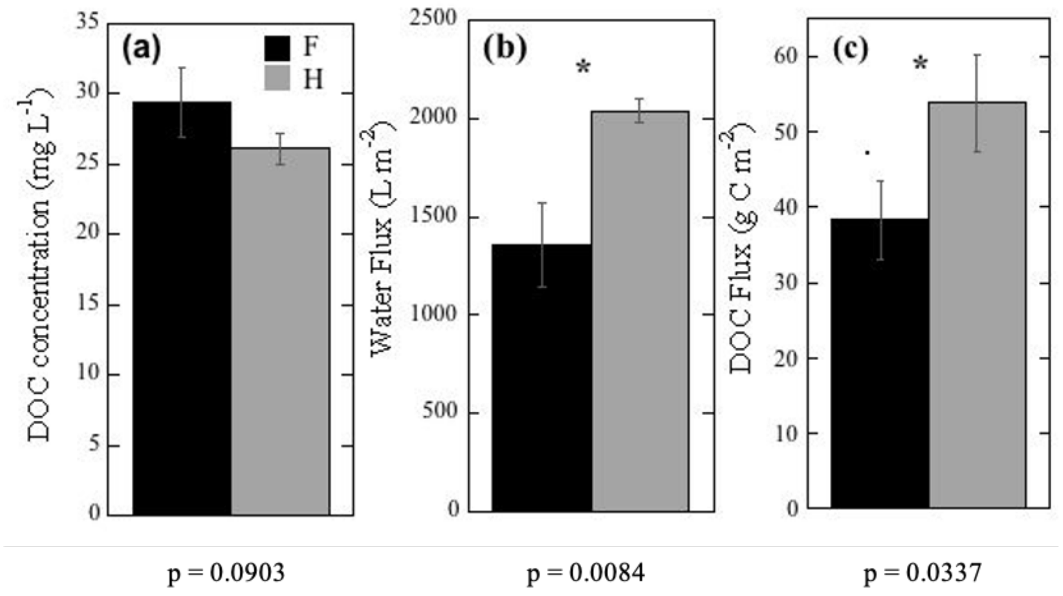
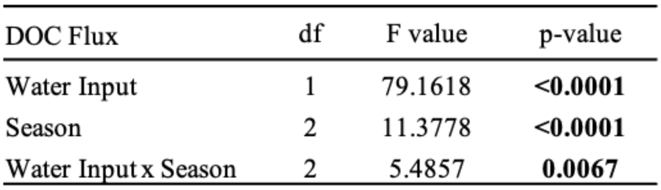


Figure 2.3: Mean annual dissolved organic carbon (DOC) concentration, water flux, and DOC flux. Volume weighted dissolved organic carbon (DOC) concentration (A), total water flux (B), and total DOC flux collected from organic horizons of forest (F) and harvested (H) plots over the entire study period. Annual values were calculated from the accumulated 29 sample collection time points taken from 12 F and 12 H passive pan lysimeters over one year from July 2013 to July 2014. Asterisks show significant differences between plot type (alpha = 0.05) determined using one-way plot nested ANOVA tests (Table S2).

O horizon of harvested plots (Figure 2.3, p=0.00836). The intra-annual DOC and water fluxes varied with collection day, with an interactive effect of plot type and collection day on both fluxes (Table 2.2A,B). Measured water fluxes were generally greater in harvested plots than forest plots on a given collection day, often correlating to greater DOC fluxes in harvested plots (Figure 2.2D,E; asterisks). The difference in water flux between plot types was significant on 8 of 30 collection days, while the difference in DOC flux between plot types was significant less often (6 of 30).

Longer periods of soil drying and low rainfall, occurring predominately during summer, corresponded with periods of little to no water flux and, consequently, little to no DOC flux in both harvested and forest plots (Figure 2.2B,D,E; shaded areas). In contrast, periods of relatively high moisture and consistent rainfall, occurring predominately in autumn, corresponded with high and consistent water and DOC fluxes. During spring snowmelt, however, when the DOC concentration was relatively low, the largest water fluxes did not result in the largest fluxes of DOC (Figure 2.2; April 8 2014 to May 1 2014). The highest DOC flux over the study period was observed in early autumn when a large rain event followed a warm period of soil drying. Soil water fluxes were negatively correlated with soil temperature (Table 2.2A) and there was a strong positive correlation between water input and both soil water and DOC fluxes measured in both plot types (Table 2.2C). There was an interaction between season and water input on DOC fluxes (Table 2.3), where a linear relationship between water input and DOC fluxes was observed in the summer (Figure 2.4A), but DOC fluxes exhibited a tapering off in autumn and snowmelt when water input to soil was high (Figure 2.4B,C).

Table 2.3: Two-way ANOVA results examining the effect of water input, season and the interaction on DOC fluxes.



DOC Flux	df	F value	p-value
Water Input	1	79.1618	**<0.0001**
Season	2	11.3778	**<0.0001**
Water Input x Season	2	5.4857	**0.0067**

2.4 Discussion

2.4.1 Hydrology drives temporal and plot type differences in DOC flux

This study revealed a 30% greater annual mobilization of DOC from O horizons in 10 year old harvested plots compared with forest plots. This was despite lower O horizon SOC stocks and C inputs from aboveground litter in harvested plots (Table 2.1). Annually, the larger flux of DOC in the harvested plots correlated to a larger annual input of water to the soil surface, larger fluxes of water through thinner O horizons, and warmer mean annual soil temperature. On weekly to monthly time scales, both forest and harvested O horizon DOC flux patterns mirrored those of water fluxes while the contribution of DOC concentration variations to observed temporal differences was less evident in DOC flux

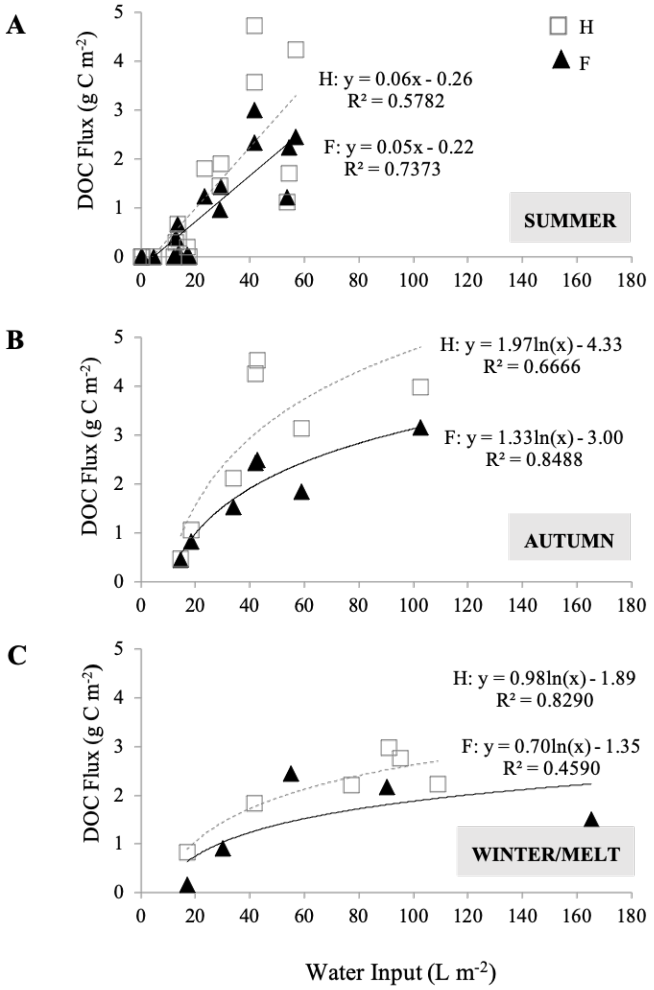


Figure 2.4: Seasonal relationship between dissolved organic carbon (DOC) fluxes and water input to the soil in mature forest (F) and harvested (H) plots. Seasons are designated as summer (a), autumn (b) and winter + snowmelt (c).

patterns (Figure 2.2D,E,F). This is additionally described in both plot types by a strong positive relationship between water input to the forest floor (as rainfall, throughfall and/or snowmelt) and DOC flux, but with no relationship between DOC flux and soil temperature (Table 2.2). Therefore, across both forest and harvested landscapes characterized by different surface soil and ecosystem properties, water input to soil is a dominant control over O horizon DOC mobilization dynamics on varying time and spatial scales. Increases in DOC fluxes from O horizons immediately following and up to 5 years after boreal forest harvesting were previously documented by lysimeter studies (Piirainen et al., 2002;

Kalbitz et al., 2004). However, to our knowledge this is the first study to demonstrate a longer lasting (10-year) harvesting effect on DOC fluxes. Harvesting results in sites becoming CO_2 sources to the atmosphere for several years. As tree growth rates increase, forests reach a compensation point where they are neither sources nor sinks of C typically within 10-20 years following boreal forest harvesting (Kurz et al., 2013). These estimates are based primarily on CO_2 efflux and biomass C sequestration with growth, but our data suggest that hydrological losses of C can also affect this compensation point, where significant differences in water and DOC fluxes between forest and harvested plots are still evident 10 years after harvesting.

To establish water input as a main driver of regional O horizon DOC flux variability, regional C budget models should be parameterized to reflect the spatial heterogeneity in mean annual precipitation (MAP) that exists across the boreal. This is supported by our results, as well as prior correlations between MAP and annual DOC fluxes across ecosystems (Michalzik et al., 2001), and is especially relevant given the large range in MAP that exists across boreal ecoregions (for example, Canada's boreal Ecoregions 173 – 1492 mm; A National Ecological Framework for Canada, 1999). Furthermore, studies examining controls on DOC content in soils at depth focus on delivery of DOC from O to mineral horizons and the subsequent mineral-OM interactions that control soil C sequestration (Clarke et al., 2007; Fröberg et al., 2011; Kalbitz et al., 2004; Rosenqvist et al., 2010). Associated conceptual models assume vertical fluxes of water and DOC (eg. Kaiser and Kalbitz, 2012). Vertically-dominated O to mineral horizon DOC fluxes may occur in some boreal systems and they may be relevant at larger spatial scales in low relief landscapes. In our moss-mantled hillslopes, however, event-specific lateral flow was likely important in over half of the measurements made as water collected by lysimeters located at the base of the O horizon exceeded total precipitation or snowmelt over the lysimeter footprint on 17 of 30 collection dates in the forest plots, and 18 of 30 in the harvested plots. Although passive lysimeters do potentially disrupt natural soil hydrological conditions, the soil hydraulic properties of the O horizons (Table 2.4), combined with continuous field measurements of O horizon soil moisture, indicate that these lysimeters captured a combination of vertical and lateral flow during many precipitation events. Water fluxes measured exceeded the total precipitation or snowmelt over the lysimeter footprint only when matric saturation of the O horizon had been reached and macropore flow was initiated (Figure 2.5). At soil moisture contents above matric saturation, capillary

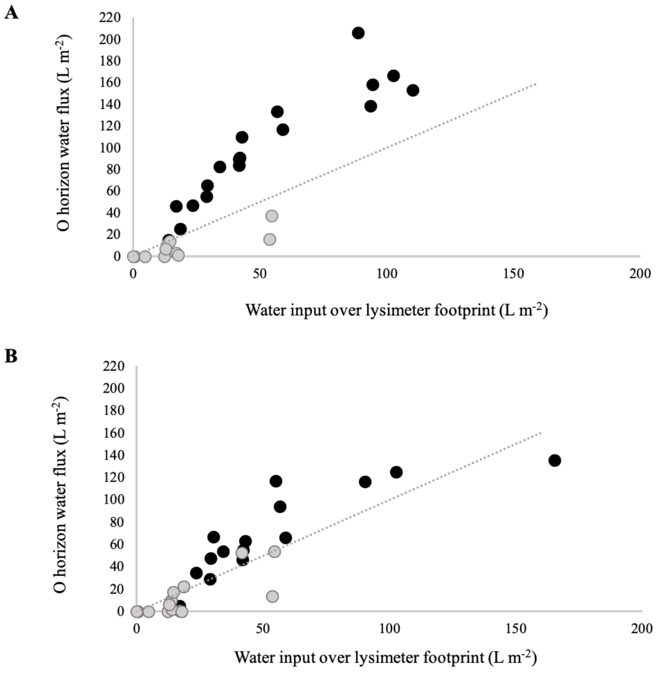
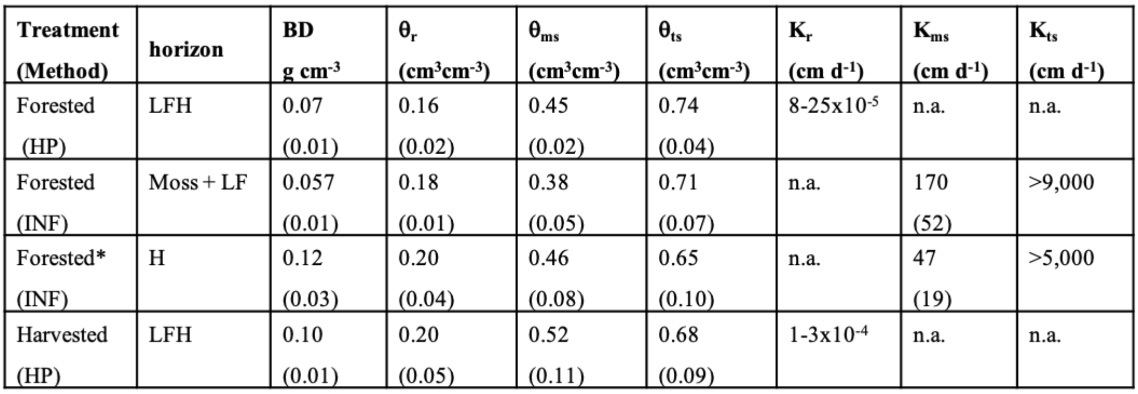


Figure 2.5: Lysimeter captured water fluxes versus water input over the lysimeter footprint in harvested (a) and forest (b) plots. Lysimeter collections made during periods when volumetric soil water content remained below soil matrix saturation (grey circles) contrast with lysimeter collections made during periods when soil matrix saturation was reached (black circles). Matrix saturation in harvested and forest plots was determined by infiltration experiments and complimented by soil evaporation measurements (see Table 2.4).

forces are ineffective and water flows uninhibited through the macropores of O horizons, flowing downslope at the base of the O horizon due to the lower hydraulic conductivity of the underlying mineral horizons. This phenomena likely drove the pipe throughflow observed at the O-mineral horizon interface in a boreal forest hillslope during snowmelt resulting in the delivery of highly acidic surface soil water to lakes (Roberge and Plamondon, 1987). Lateral transport of water and solutes as facilitated by macropore flow is recognized as a potentially important feature controlling landscape transport of solutes in forest hillslope and stream catchment studies (Kaiser and Guggenberger 2005; van Verseveld et al. 2008; Terajima and Moriizumi 2013; Laine-Kaulio et al. 2014). While modelling of water and solute transport continues to evolve and incorporate macropore flow (Beven and German, 1982 and 2013), models are limited to modelling of mineral soil and do not explicitly define porous O horizons that are typically an important source of DOC in boreal forest landscapes. We advise that direct measurement and incorporation of the specific hydrologic role of O-horizons is essential because they represent both a hydrologically unique layer and a *hot spot* for DOC mobilization. This will improve estimates of DOC mobilization and redistribution dynamics at the landscape scale.

Table 2.4: Average soil hydraulic parameters of organic horizons. Data was obtained from HYPROP (HP) evaporation apparatus for unsaturated conditions and falling head infiltration (INF) tests for matrix-saturated and totally-saturated (macropore infiltration) conditions. Both tests were made on intact cores and standard deviations are provided in parentheses (n = 6). Live and senescent moss was removed for the HP analysis, but not the INF analysis (see "horizon" column). BD = bulk density, ϑ_r = water content at residual saturation, ϑ_{ms} = water content at matrix saturation, ϑ_{ts} = water content at total saturation, K_{ms} = hydraulic conductivity at matrix saturation, K_{ts} = hydraulic conductivity at total saturation. Results from INF were used to calibrate continuous field measurements (see Table S8).



Treatment (Method)	**horizon**	**BD g cm^{-3}**	**θ_r (cm^{3}cm^{-3})**	**θ_{ms} (cm^{3}cm^{-3})**	**θ_{ts} (cm^{3}cm^{-3})**	**K_r (cm d^{-1})**	**K_{ms} (cm d^{-1})**	**K_{ts} (cm d^{-1})**
Forested (HP)	LFH	0.07 (0.01)	0.16 (0.02)	0.45 (0.02)	0.74 (0.04)	8-25x10^{-5}	n.a.	n.a.
Forested (INF)	Moss + LF	0.057 (0.01)	0.18 (0.01)	0.38 (0.05)	0.71 (0.07)	n.a.	170 (52)	>9,000
Forested* (INF)	H	0.12 (0.03)	0.20 (0.04)	0.46 (0.08)	0.65 (0.10)	n.a.	47 (19)	>5,000
Harvested (HP)	LFH	0.10 (0.01)	0.20 (0.05)	0.52 (0.11)	0.68 (0.09)	1-3x10^{-4}	n.a.	n.a.

*INF measurements of Forested H was used to represent the Harvested O layer. See methods for details.

2.4.2 DOC flux and water flux relationship varies with seasonal environmental change and suggests an interactive temperature control

Despite the control of water input rate on DOC fluxes, the relationship between DOC flux and water flux varied at the seasonal scale (Figure 2.4; Table 2.3). Soils of both plot types appeared to be flushed of DOC during periods of high, continual leaching and low temperatures (Figure 2.2), suggesting that the seasonally variable production of DOC and/or water soluble organic carbon (WSOC) is an important secondary control. Some field studies have shown that soil DOC concentrations remain constant and do not become more dilute with increasing soil water fluxes, suggesting that the pool of WSOC is not easily exhausted in those systems (Kalbitz et al., 2007; Klotzbücher et al., 2014). This leads to proportional increases in DOC flux with increasing water flux and therefore, a water limitation on DOC mobilization. While summer (Figure 2.4A), and likely winter, DOC fluxes in this study were similarly water-limited, autumn and spring snowmelt fluxes exhibited a tapering off of DOC fluxes during periods of highest water input (Figure 2.4B,C), suggesting a production-limitation during autumn and snowmelt.

DOC flux was calculated as the product of DOC concentration and solution volume for each measurement period, therefore, the highest periods of DOC flux occur when conditions support relatively high values of both terms. This occurred most frequently during late summer/early autumn and ecologically requires the combination of: (1) the production of water-soluble organic carbon (WSOC) or DOC via temperature sensitive mechanisms such as SOM and/or litter decomposition rhizodeposition, and microbial biomass turnover (Christ and David, 1996; Kalbitz et al., 2007; Weintraub et al., 2007), and (2) sufficient water inputs to result in a soil water flux that mobilizes or extracts DOC from O horizons. Soil water fluxes were negatively correlated with soil temperature in this study (Table 2.2A), likely driven by the seasonal temperature dependence of net water input and evapotranspiration, while DOC concentration was positively correlated with soil temperature. Therefore, the seasonality of DOC flux involves an interactive temperature effect, where temperature dependent biogeochemical processes and temperature dependent soil water fluxes interact to form seasonally unique combinations or scenarios important to a predictive understanding of these fluxes.

2.4.3 Water Limited Scenarios: Summer and Winter

Fluxes of water and DOC were dynamic on the weekly to monthly scale during all seasons except winter (Figure 2.2E,F), revealing that flux conditions can occur at all times of the year in these sites, except during periods of deep, consistent snowpack which limits water input to the soil and consequently, DOC mobilization. Summer also exhibited a water limitation on DOC mobilization but on a shorter time scale, alternating between weekly periods of no water and DOC flux and periods of large water and DOC fluxes. While we detected no relationship between DOC flux and soil moisture using the whole dataset (Table 2.2B), antecedent soil moisture can affect the proportion of the water input that results in a water and DOC flux in the summer when soil drying-rewetting cycles were common (Figure 2.2; grey shaded bars), although this does not appear to be a driving factor throughout the year in these plots. In summer, when CO_2 efflux rates were high but DOC fluxes were intermittent, CO_2 was in part, a larger loss of soil C because insufficient water input limited mobilization of DOC from O horizons. Without mobilization, DOC is more readily lost via respiration (Moore et al., 2008). In early autumn however, the elevated water flux, cooler temperatures, and decreasing CO_2 efflux rates, favour an increasing proportion of the SOC pool being mobilized as DOC and lost to downstream C pools either in mineral soil or further to groundwater and headwaters.

2.4.4 DOC Production Limited Scenarios: Autumn and Snowmelt

With continuous leaching and decreasing soil temperatures, late autumn water inputs resulted in a decrease in DOC concentrations and DOC fluxes, such that soils appear to be flushed of the WSOC or DOC pool just prior to snowpack development. Thus the availability of the extractable DOC pool in these soils during the snowpack and subsequent snowmelt period was likely much reduced by high autumn water input at low soil temperatures. Spring snowmelt captured during this study year followed a winter of constant snow cover and contributed approximately 31% of the annual water input to the soil, and 20% of the annual DOC flux, but occurred over a period that represented only 13% of the year. Despite representing the largest hydrological event during this study year, the large water flux over a short time period combined with relatively low soil temperatures and previously flushed soils, resulted in dilute leachate (low DOC concentration) and a smaller contribution to the annual DOC flux in relation to early autumn fluxes.

2.4.5 Climate change impacts on soil conditions and precipitation patterns will affect DOC fluxes

This study shows that DOC flux variation is well described by water flux variation, but that gradual flushing of O horizons occurs during consistent leaching events throughout autumn as soil temperatures decrease. These seasonal trends suggest that the projected increases in precipitation at mid to high latitudes in the northern hemisphere (Kirtman et al., 2013) can result in proportional increases in DOC fluxes in the summer and early autumn when soil temperatures are warm, but that DOC or water-soluble OC (WSOC) pools are depleted during seasonal decreases in soil temperature. In order for increasing water fluxes to result in increased losses of DOC they must therefore be met with increased production of DOC/WSOC; a process dependent on how increases in precipitation are seasonally distributed. Two potential mechanisms of increased WSOC production that are linked to reductions in snowpack are the increased occurrence of winter rainfall and soil frost. No soil freezing occurred under the consistently deep snowpack conditions observed during winter in this study. With warm winter conditions expected to become more frequent in northern regions, melting and reforming of the snowpack over winter will have consequences for soil exposure and frost, as well as the frequency and magnitude of winter-time water flux events. Similar to soil drying-rewetting events (Fierer and

Schimel, 2002), soil freeze-thaw cycles have been shown to increase soil DOC concentrations by disturbing soil, root and microbial structures (Haei et al., 2013; Schimel and Clein, 1996). Increased winter rainfall and mid winter snowmelt events that drive larger winter soil water fluxes, in combination with soil freeze-thaw events that increase production of WSOC can therefore contribute to future increases in wintertime mobilization of DOC. Changing snowpack dynamics is therefore one possible mechanism of increasing river DOC export trends in northern temperate watersheds that are specifically attributed to increases in wintertime DOC exports (Huntington et al. 2016). These results suggest that the effect of climate change on boreal forest DOC fluxes will depend on the redistribution of seasonal precipitation and changes to precipitation form. In addition, this study highlights that defining macropore-driven lateral water flow dynamics, particularly at the O to mineral horizon interface, can help define the role of DOC at the landscape scale.

Chapter 3

Seasonal controls override the effects of forest harvesting on the composition of dissolved organic matter mobilized from boreal forest soil organic horizons

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Author Contributions:KAE and SEZ designed the study with input from KLB. KLB and KAE designed the lysimeters and planned their installation as well as installation of all environmental monitoring equipment. KLB collected and analysed the lysimeter, environmental monitoring and soil properties data. KLB prepared the paper, with editing from SEZ and KAE.

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Abstract

Dissolved organic matter (DOM) mobilized from the organic (O) horizons of forest soils is a temporally dynamic carbon (C) and nutrient flux, and the fate of this flux in downstream pools is dependent on water flow paths as well as the chemical composition of DOM. Here, we present observations of the composition of DOM mobilized weekly to monthly from O horizons in mature forest (F) and adjacent harvested (H) plots. The study site was experimentally harvested, without replanting, 10-years prior to this study. Thus, the plots differ significantly in terms of forest stand and soil structure, and interact differently with the regional hydrometeorological conditions. This presents an opportunity to investigate the role of forest structure relative to hydrometerological conditions on soil DOM mobilization. On an annual basis, fluxes of total dissolved nitrogen (TDN) and dissolved organic nitrogen (DON) were largest from the warmer and thinner O horizons of the H plots compared to the F plots, however, neither phosphate (PO_4^{3-}) or ammonium (NH_4^+) fluxes differed by plot type. On a short-term basis in both H and F plots, all fluxes were positively correlated to water input, and all concentrations were positively correlated to soil temperature and negatively correlated to water input. Soil moisture was only correlated to the C:N of DOM. These results suggest common seasonal controls on DOM mobilization in the two plot types. Optical characterization of seasonally representative samples additionally supported a stronger control of season over harvesting. One of the most significant of these controls was the insulating role of the snowpack throughout winter, which maintained a stable soil temperature of approximately 2°C in both plots over the study year. The chemical character of DOM mobilized during winter and snowmelt; lower C:N, higher $SUVA_{254nm}$ and lower molecular weight of CDOM, was representative of relatively more decomposed DOM, compared to that mobilized in summer and autumn. This shows that the decomposition of soil organic matter underneath a consistently deep snowpack is a key determinant of the composition of DOM mobilized from O horizons during winter and the hydrologically significant snowmelt period. Despite the higher proportion of aromatic DOM in the snowmelt samples, the rapid delivery of DOM

from O to mineral horizons suggests that snowmelt is not likely to be a significant period of DOM sequestration by minerals. Rather, the slow and relatively infrequent mobilization of high molecular weight, high C:N DOM delivered during summer is a more likely period of significant mineral soil sequestration of DOM. Understanding these dynamics improves our ability to accurately portray the role of O horizon DOM in linking soils to aquatic systems, as well as the response of soil organic matter and T-A fluxes to a rapidly changing climate in northern latitudes.

3.1 Introduction

Dissolved organic matter (DOM) mobilized from organic horizons of forest soils represents an ecologically significant source of carbon (C) and nutrients both within forest catchments (Qualls and Haines, 1991), and from soils to aquatic systems (Jansen et al., 2014). The fate of mobilized soil DOM is influenced by both water flow dynamics (rate and pathways) and the chemical composition of DOM (Roulet and Moore, 2006), although the interaction of these two factors is not often captured in soil studies. The composition of mobilized organic horizon DOM is the net result of production and uptake processes, as well as the relative solubility of organic matter inputs from different sources. While soil extractions provide valuable information on potential sources, bioavailability, and production mechanisms of soil DOM (i.e. Wickland et al., 2007; Moore et al., 2008; Jones and Kielland, 2012; Hensgens et al., 2020), they cannot capture the interaction of these factors with local hydrometeorological conditions important to understanding the net movement of DOM *in situ*. Measurements that incorporate the role of soil hydrology with DOM mobilization place knowledge gained from extraction studies into the larger catchment scale context. For instance, these measurements can more directly inform regional chromatography (i.e. Shen et al., 2015) and terrestrial-to-aquatic carbon flux (i.e. Tank et al., 2018) conceptual models, which would further allow us to assess the impacts of disturbances such as harvesting and climate change.

Forest C and nitrogen (N) cycles are tightly linked and the C:N of bulk soil provides clues about ecosystem functioning and the bioavailability of soil organic matter. Similarly, the C:N of DOM is considered a measure of DOM bioavailability (McDowell et al., 2004; McGroddy et al., 2008). However, while C:N of DOM correlates to C:N of soil in some studies (Gödde et al., 1996; Michalzik and Matzner, 1999; Aitkenhead and McDowell, 2000), it does not in others (Cortina et al., 1995; Michel and Matzner, 1999). The mobilization of DOC relative to DON is correlated on an annual basis (Michalzik et al., 2001), but whether this correlation holds across seasons is not known and could help explain the discrepancies in the relationship between C:N of soil and C:N of DOM. Additionally, boreal forests accumulate particularly large amounts of carbon in surface layers because of temperature-limitations on soil organic matter decomposition and the recalcitrance of coniferous tree litter (Hensgens et al., 2020). Nitrogen-limitations can also affect decomposition and soil C accumulation (Averil and Waring, 2017), and may explain why the C:N of boreal soil organic horizons is higher in areas not affected by industrial N deposition (for instance, Alaskan compared to Swedish boreal forests), with likely ramifications on soil DOM. These dynamics are further impacted by snow-cover, especially during seasonal transition periods (Groffman et al., 2018), but the type of snowpack change is regionally variable with differing effects on the underlying soil (Stark et al., 2020).

Spectroscopic characterization (absorbance and fluorescence) of chromophoric DOM (CDOM) is often used to describe DOM compositional differences and identify terrestrial DOM sources in surface water (Helms et al., 2008; McKnight et al., 2001; Jaffe et al., 2008; Fellman et al., 2010; Berggren and del Giorgio, 2014). They have also been used to assess the compositional variability of terrestrial DOM. In litter incubation experiments, for instance, Specific Ultraviolet Absorbance (SUVA) of leached spruce needles increased during decomposition because of increased solubility of lignin as it became more degraded (Hansson et al., 2010; Klotzbücher et al., 2013). Similarly, an increase in aromaticity of soil DOM, but a decrease in C:N of DOM, was observed in snowmelt simulation performed over soil columns collected from both coniferous and deciduous sites (Campbell et al., 2014), and the aromatic content of O horizon DOM from different forest types in Sweden were found not to differ (Fröberg et al., 2011). Variations in aromaticity of O horizon DOM suggests variation in mineral stabilization potential of DOM in mineral soils. For instance, an input of aromatic compounds from O horizons to the mineral soil is more likely to result in formation of organo-mineral complexes that stabilize OM, than an input of mobile, hydrophilic compounds such as carbohydrates (Guggenberger and Zech, 1993; Kalbitz and Kaiser, 2012; Kramer et al., 2012; Shen et al., 2015). However, *in situ*, the consequences of these transformations are dependent on the rate and pathways of water and DOM. Clarification is needed on the impacts of both the rate and composition of mobilized DOM to better understand mineral stabilization versus export potential of soil DOM from upland forests under varying hydrometeorological conditions.

The large and small-scale effects of hydrometeorological conditions on DOM dynamics can be confounded by effects of disturbances, such as fire, insects and forest harvesting. Forest harvesting is a significant anthropogenic disturbance in boreal forests with known impacts on soil moisture and temperature during the growing season and increased export of water and DOM (Kreutzweiser et al., 2008). Mid- to long-term effects on soils in naturally regenerating forest are not well-known, but are likely significant in clear-cut boreal black spruce forests that can remain open for long periods of time in the absence of wildfire. As seasonal and long-term harvesting effects on DOM dynamics are both potentially significant but confounding, our objective with this study was to parse out the main effects of each. We frequently sampled mobilized soil DOM using a passive pan lysimeters study in open harvested plots compared to adjacent mature black spruce forest plots. Previously, we demonstrated that the thickness of the organic horizon had reduced by almost 50% in the open harvested plots, that the quantity of DOC mobilized in the harvested plots was larger than in the forested plots, and that the relationship between water fluxes and mobilized DOC varied seasonally (Bowering et al., 2020). Here, we describe the temporal and spatial variability of DOM composition mobilized from soil organic horizons to better understand the controls of forest stand and soil structure relative to short-term hydrometeorological variability. This information will help identify the "top-down" controls on the storage of carbon and nutrients in boreal forest mineral soils and export to aquatic systems, and highlight the hot spots and moments of DOM mobilization that are likely sensitive to boreal forest climate change.

3.2 Materials and Methods

3.2.1 Site Description

This study was conducted in an experimental forest at the Pynn's Brook Experimental Watershed Area (PBEWA) located near Deer Lake, western Newfoundland and Labrador, Canada. (48° 53'14" N, 63° 24' 8" W). The forest is mesic relative to other areas of the boreal ecozone and is dominated by black spruce (*Picea mariana*). The surrounding boreal landscape is characterized by a mix of age classes resulting from a history of periodic disturbance, including that from forest harvesting. The region receives approximately 1095 mm of precipitation annually with a mean annual temperature of 3.6°C (Environment Canada Climate Normals, Deer Lake Airport 1981–2010). The site consists of 2 hectares divided into eight 50 x 50 m plots. Four of the plots were left un-harvested and four were randomly selected for clear-cut harvesting. The four clear-cut plots were harvested on July 07–10, 2003 using a short-wood mechanical harvester, with minimal disturbance to the underlying soil and with any deciduous trees left standing. Further information on site preparation and conditions can be found in Moroni et al., 2009. Following the common forestry practices in Newfoundland and Labrador, the harvested plots were not replanted following clear-cutting. Moss coverage persisted in the harvested plots, with the addition of naturally regenerated herbs and shrubs and few young conifers at much lower density than the adjacent mature stands. The two treatments will be referred to as harvested (H) and mature forest (F) throughout.

3.2.2 Lysimeter Installation and Sample Collection

Passive pan lysimeters were installed just underneath the organic horizon. Each lysimeter has a 0.12 m^2 footprint and collects water percolating through the O horizon with a maximum solution collection capacity of 25 L. The lysimeters were designed using reported recommendations for achieving accurate volumetric measurements of soil leachate (Radulovich and Sollins, 1987; Titus et al., 1999). A detailed description of the lysimeter design can be found in Figure 2.1.

Installation of lysimeters began in July 2012 and was completed the following spring in May 2013. Four lysimeters were installed in three plots of each treatment for a total of 12 mature forest (F) lysimeters and 12 harvested (H) lysimeters. Collection began in July 2013 and sampling of all lysimeters of both treatments (n = 24) was carried out on a weekly to monthly basis, with the exception of the winter season when only one collection was made, for a total of 27 sampling days within the study year. Lysimeter samples were stored in a cooler immediately following collection. Once transported back to the laboratory the pH of each sample was measured, and then samples were filtered using pre-combusted GF/F (0.45 µm pore size) Whatman filter paper, preserved with mercuric chloride within 24 hours of collection, and stored at 4°C in the dark until analysis.

3.2.3 Environmental Monitoring

Three soil temperature and moisture probes per treatment (Decagon ECH2O -TM) were installed mid- organic horizon at approximately 5-cm depth, and two were installed in the mineral layer at approximately 15-cm depth.. Soil moisture was measured as % volumetric water content (VWC). One tipping bucket rain gauge (RST Instruments Model TR-525) was installed in an open area on site to monitor local rain and air temperature. Data from this tipping bucket were compared with regional rainfall and air temperature (T) reported by Environment Canada at the Deer Lake Airport (49°13’00” N, 57°24’00” W) approximately 50 km away, and Deer Lake Airport data was a good predictor of the

PBEWA rainfall and air T on a weekly basis ($R^2 = 0.882$, $p<0.0001$). Regional data from the Deer Lake Airport were used to fill a gap in our onsite daily rainfall and mean daily air temperature data between July 7th and 24th, 2013. Snowmelt water input was estimated using changes in snow depth between each lysimeter collection day measured near each lysimeter in both H and F. The average snow depth change by treatment was multiplied by an estimated maritime snow density of 0.343 g cm-3 (Sturm et al. 2010) to provide an estimated snowmelt water input value. Snowmelt water input estimates were combined with rain (in harvested) or throughfall (in mature forest) where applicable to give a total water input to the O horizon over each collection period, different from the soil water fluxes independently measured by the lysimeters. Observations of significant lateral flow along the O to mineral horizon interface have been previously reported (Bowering et al., 2020).

3.2.4 Chemical Analysis and Flux Calculations

The DOC and TDN concentration of each lysimeter sample collected was measured using a high-temperature combustion analyzer (Shimadzu TOC-V and TN analyzer, Japan). Nitrate (NO_3^-; detection limit = 0.01 mg N L^{-1}), ammonium (NH_4^+; detection limit = 0.004 mg N L^{-1}) and phosphate (PO_4^{3-}; detection limit = 0.01 mg P L^{-1}) were measured using QuickChem Methods No. 10-107-04-1-B, 10-107-06-2-A and 10-115-01-1-A respectively, using flow injection analysis (Lachat QuickChem 8500 Series 2, USA). No NO_3^- was detected using this colorimetric method. Total dissolved phosphorus (TDP; detection limit = 2.9 µg L^{-1}), aluminum (Al; detection limit = 1.1 µg L^{-1}) and iron (Fe; detection limit = 0.3 µg L^{-1}) were measured using Inductively Coupled Plasma – Optical Emission Spectroscopy (Perkin Elmer 5300 DV, USA). These measured concentrations, along with the total volume collected by lysimeters, the number of collection days, and the lysimeter collection area were used to calculate a flux (g solute m^{-2} d^{-1}).

3.2.5 Seasonal Designations

Lysimeter collections were grouped into four distinct hydrological periods throughout the year described by observed soil moisture, precipitation, soil temperature patterns, together with water flux dynamics measured via the lysimeters as shown in Bowering et al., 2020. Briefly, summer is characterized by fluctuations in soil drying and rewetting, and frequent periods of no O horizon water fluxes. The transition to autumn is described by more consistent soil moisture and frequent precipitation events that resulted in frequent soil water fluxes as temperatures dropped. Winter was characterized by a consistent snowpack that insulated the soil, where soil temperatures were maintained above 0°C despite sub-zero atmospheric temperatures. A very short-term melting event resulted in only a small delivery of water to the soil and therefore, only small cumulative water flux throughout the whole winter. The snowmelt period is characterized by rapid water input to soil, wet soils and increasing soil temperatures.

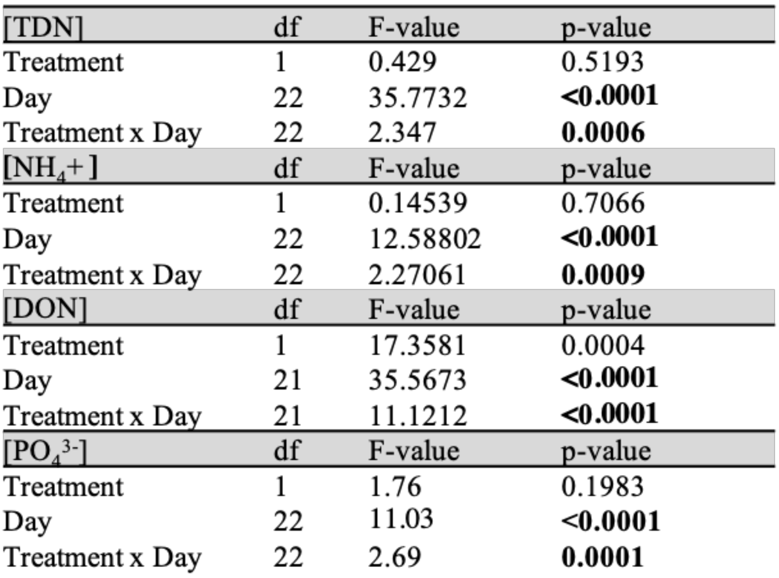
3.2.6 Absorbance Properties

A subset of lysimeter samples from forest and harvested plots was selected to broadly represent the four seasons (Table S10). Each sample was diluted to approximately 15 mg DOC L^{-1} for absorbance measurements. An absorbance scan from 200–800 nm was performed on each sample in a 1 cm cuvette using a Perkin Elmer Lambda UV/Vis spectrophotometer following a blank consisting of NanoUV water (Barnsted Inc). Specific UV absorbance (SUVA) was calculated using the sample absorbance at 254 nm normalized to DOC concentration ($SUVA_{254nm}$). Spectral slopes of the 275–295 nm low molecular weight (LMW) region and 350–400 nm high molecular weight (HMW) region were calculated from each absorbance spectra based on Helms et al., 2008, and a slope ratio (Sr) indicative of the LMW:HMW of CDOM was used to describe changes in relative molecular weight of CDOM. The absorbance spectra were corrected for potential Fe(III) interference, using correction factors based on Poulin et al., 2014, but derived for these specific sample types. Although the specific speciation of Fe was not measured, a 100% Fe (III) was assumed to facilitate an estimate of the highest possible interference given the oxic nature of samples when analyzed in the laboratory. A negligible effect of Fe on the absorbance measurement was observed for these samples (Fe represented 0.4 – 0.6% of total sample absorbance per collection date). Seasonally representative absorbance properties ($SUVA_{254nm}$, $SS_{275-295}$, $SS_{350-400}$, and Sr), the C:N of DOM, and DOC:Fe were included in a principal component analysis to explore the predominant variables contributing to the effect of treatment (Figure 3.4A) relative to season (Figure 3.4B).

3.2.7 Statistical Analysis

All statistical analyses were performed using RStudio version 1.0.136. A repeated measures linear mixed effects models (RM-LMM) were used to assess the effects of collection day, and the interaction between sampling date and treatment on the fluxes and concentrations (Tables 3.2 and 3.1) using the ‘nlme’ package (Penheiro, 2020). Post-hoc Tukey tests using the ‘lsmeans’ package (Lenth, 2018) were used to determine significant differences between H and F treatments on individual collection days (Figures 3.1 and 3.2; asterisks). Further RM-LMMs were used to assess the effects of collection day and treatment on absorbance properties and metals (Table 3.4), and to assess the effects of season and treatment on DOM fluxes (Table 3.5). One-way ANOVAs were used to determine differences in total annual fluxes and mean concentrations between H and F treatments over the entire study period (Tables S8 and S9). Annual fluxes by treatment are shown in Figure 3.1 and Figure 3.2 boxplots. Correlation testing was used to examine the association between weekly to monthly lysimeter captured fluxes and concentrations, and environmental predictor variables: mean soil temperature, mean soil moisture and total water input (Table 3.3). Multiple regressions were not used due to the multi-collinearity of the predictor variables, which affected the estimated regression parameters (Quinn and Keough, 2002). Individual Pearson correlations, however, were used here to evaluate the degree of association between variables within the dataset. A Bonferroni correction was applied in the evaluation of these correlations to reduce the type I error. A principal component analysis was performed using the ggfortify (Horikoshi, 2020) and factoextra (Kassambara, 2020).

Table 3.1: Repeated measures ANOVA results assessing the effect of collection day and the interaction with treatment on lysimeter concentrations. Total dissolved nitrogen (TDN), ammonium (NH_4^+), dissolved organic nitrogen (DON), the ratio between NH_4^+ and TDN, the ratio between dissolved organic carbon and DON (DOC:DON) and orthophosphate (PO_4^{3-}).



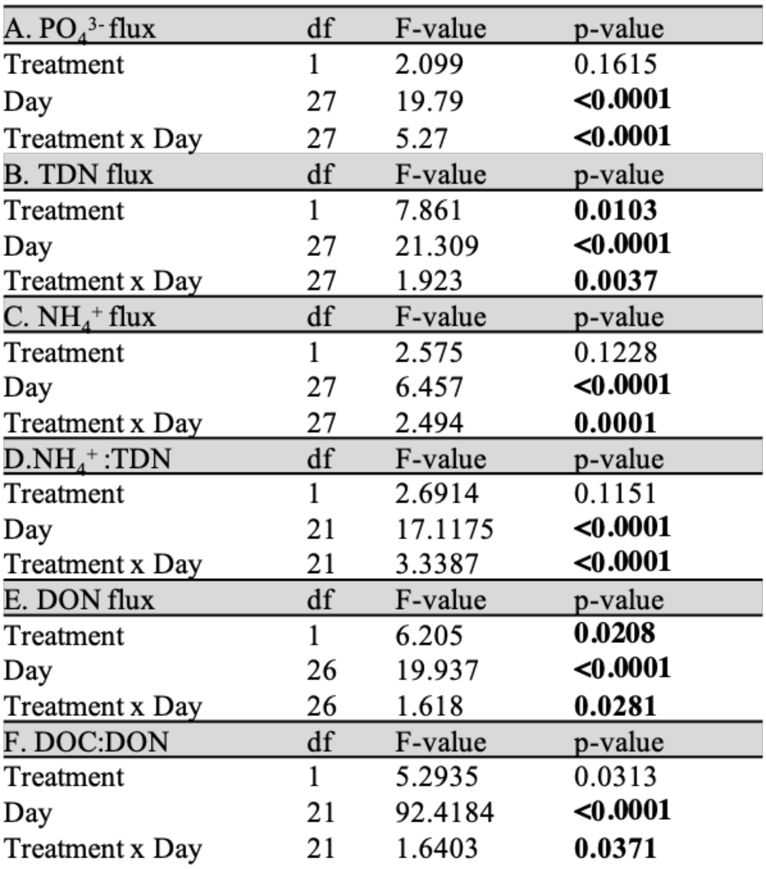
[TDN]	df	F-value	p-value
Treatment	1	0.429	0.5193
Day	22	35.7732	**<0.0001**
Treatment x Day	22	2.347	**0.0006**
[NH_4+]	df	F-value	p-value
Treatment	1	0.14539	0.7066
Day	22	12.58802	**<0.0001**
Treatment x Day	22	2.27061	**0.0009**
[DON]	df	F-value	p-value
Treatment	1	17.3581	0.0004
Day	21	35.5673	**<0.0001**
Treatment x Day	21	11.1212	**<0.0001**
[PO_4^{3-}]	df	F-value	p-value
Treatment	1	1.76	0.1983
Day	22	11.03	**<0.0001**
Treatment x Day	22	2.69	**0.0001**

3.3 Results

3.3.1 Intra-annual fluxes and concentrations in harvested and forest plots

The intra-annual fluxes and concentrations of PO_4^{3-}-, TDN, NH_4^+, DON as well as NH_4^+:TDN and C:N of DOM were variable on a weekly to monthly basis (Figures 3.1 and 3.2), indicated by the significant effect of collection day ($p<0.001$; Table 3.2). An effect of treatment was detected for DON fluxes only ($p = 0.0208$). There was an interactive effect of treatment and day on all fluxes and concentrations (Tables 3.2 and 3.1) though

Table 3.2: Repeated measures ANOVA results assessing the effect of collection day and the interaction with treatment on weekly to monthly fluxes. Total dissolved nitrogen (TDN), ammonium (NH_4^+), dissolved organic nitrogen (DON), and orthophosphate (PO_4^{3-}). Post hoc least squares means tests used to determine when significant treatment effect occurred (indicated with *asterisks* in Figure 3.1.



A. PO_4^{3-} flux	df	F-value	p-value
Treatment	1	2.099	0.1615
Day	27	19.79	**<0.0001**
Treatment x Day	27	5.27	**<0.0001**
B. TDN flux	df	F-value	p-value
Treatment	1	7.861	**0.0103**
Day	27	21.309	**<0.0001**
Treatment x Day	27	1.923	**0.0037**
C. NH_4^+ flux	df	F-value	p-value
Treatment	1	2.575	0.1228
Day	27	6.457	**<0.0001**
Treatment x Day	27	2.494	**0.0001**
D.NH_4^+:TDN	df	F-value	p-value
Treatment	1	2.6914	0.1151
Day	21	17.1175	**<0.0001**
Treatment x Day	21	3.3387	**<0.0001**
E. DON flux	df	F-value	p-value
Treatment	1	6.205	**0.0208**
Day	26	19.937	**<0.0001**
Treatment x Day	26	1.618	**0.0281**
F. DOC:DON	df	F-value	p-value
Treatment	1	5.2935	0.0313
Day	21	92.4184	**<0.0001**
Treatment x Day	21	1.6403	**0.0371**

the effect of day exhibited p-values much lower than the interaction in the case of TDN fluxes, DON fluxes and C:N of DOM.

All concentrations were positively correlated to soil temperature (Table 3.3A), except for DON in forested treatment, and all concentrations were negatively correlated with water input (Table 3.3C), except for PO_4^{3-} in both treatments and NH_4^+ in H. All fluxes were positively correlated to the water input into the soil (Table 3.3C), except NH_4^+ and PO_4^{3-} in H. No relationship was observed between concentrations and fluxes with soil moisture, except DOC concentration in H (Table 3.3B). Soil moisture was negatively correlated with the C:N of DOM in both plots.

There was an effect of collection day on all absorbance properties (Table 3.4A-D; $p<0.001$), and an effect of treatment on SUVA only ($p = 0.0033$). An interactive effect was observed for $SS_{275\text{-}295nm}$ ($p = 0.001$) and $SS_{350\text{-}395nm}$ ($p = 0.0045$). There was an effect of collection day on DOC:Fe (Table 3.4G; $p<0.001$) and no effect of harvesting. There was an effect of harvesting on DOC:Al (Table 3.4H; $p=0.0247$) and no effect of collection day.

The optical properties of CDOM in snow, collected as a bulk snow core of the entire profile just prior to snowmelt, contrasted with that of the lysimeter samples S10. The snowmelt $SUVA_{254nm}$ values were lower than all lysimeter samples and the LMW spectral slope ($SS_{275\text{-}295nm}$) was higher than lysimeter samples collected during snowmelt. The HMW spectral slope ($SS_{350\text{-}395nm}$) of snow was higher in F than H, and was higher in F snow samples than F lysimeter samples. The large differences in HMW spectral slope between treatments, compared to the LMW spectral slope, resulted in an elevated Sr value for the H snow (2.60) in comparison to the F snow (0.69).

3.3.2 Annual fluxes and concentrations in harvested and forest plots

Total annual flux of TDN and DON was largest from the organic (O) horizons of the harvested (H) compared to mature forest (F) treatment (Figure 3.1D,E and S1), consistent with DOC, and total water (soil solution) fluxes previously reported (Bowering et al., 2020). In both treatments DON comprised approximately 85% of the annually mobilized total dissolved nitrogen (TDN) flux. Ammonium (NH_4^+) was the predominant form of inorganic nitrogen (N), with no detectable nitrate. The annual NH_4^+ flux and the annual ratio of C:N of DOM were not different between H and F treatments. The C:N OF DOM in the H was lower than the C:N of the O horizon soil from which it was derived, while the C:N of DOM in F was similar to the C:N of the O horizon soil (Figure 3.2B). Despite treatment differences in annual fluxes (Figure 3.1 and Table S1), the average annual concentrations of all solutes did not differ between treatments (Table S2).

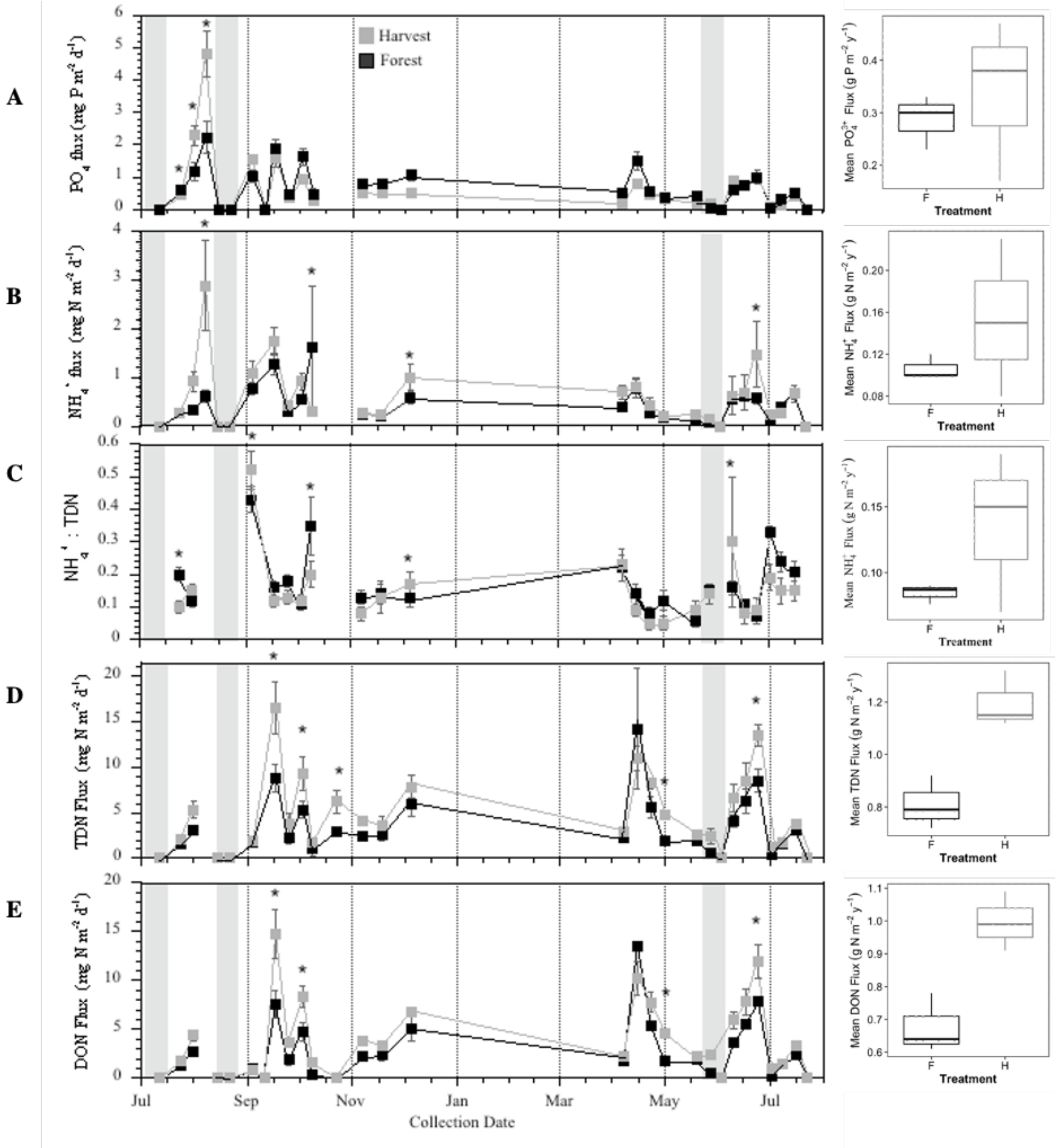
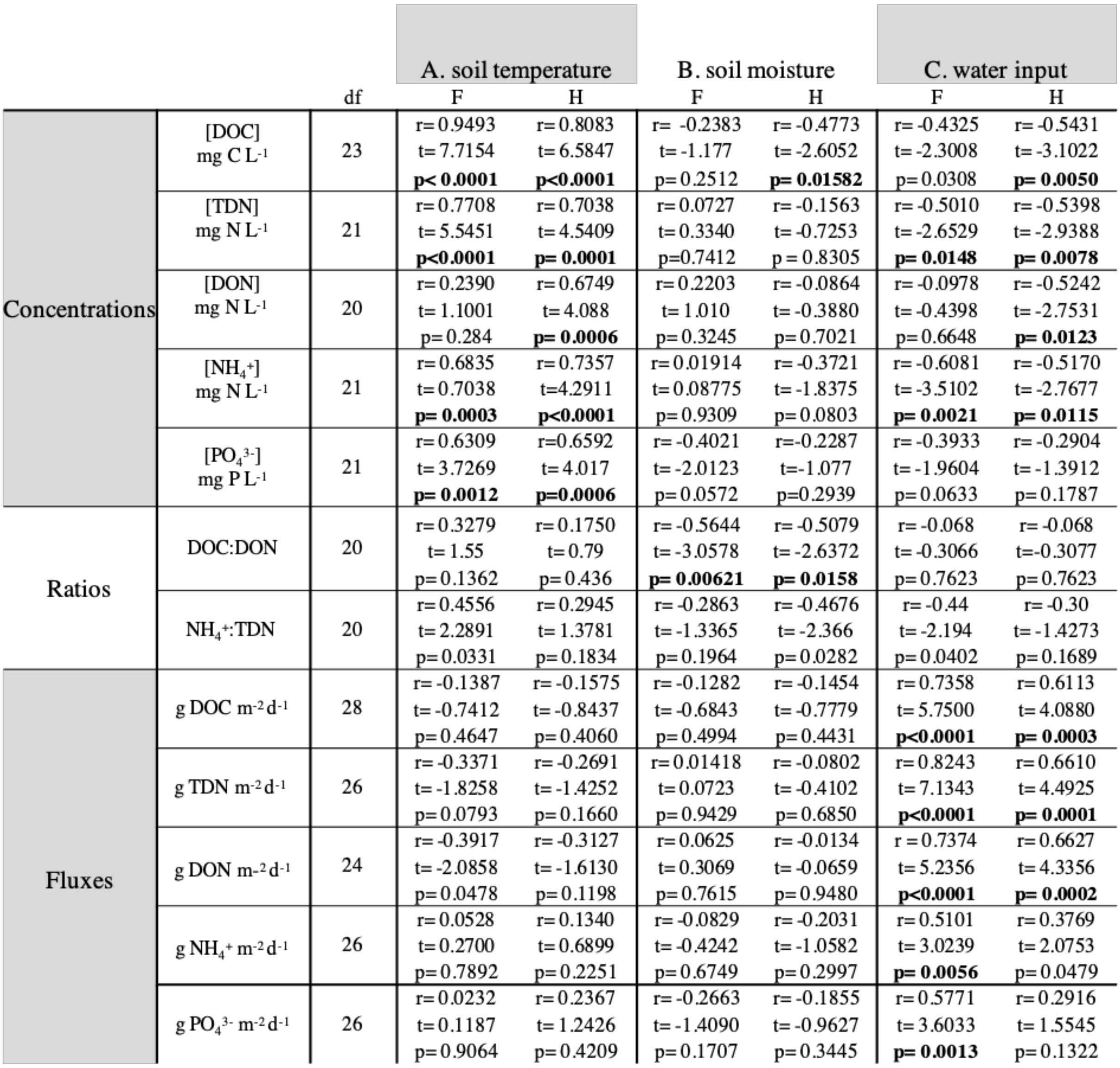


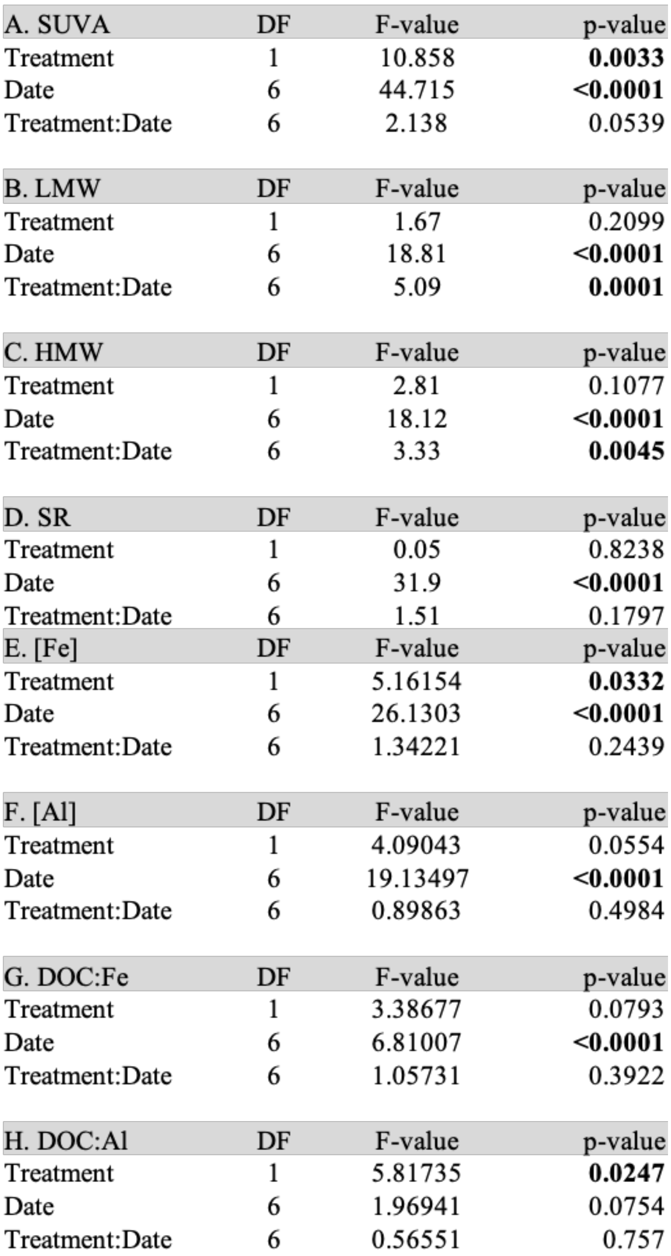
Figure 3.1: Intra-annual variation of lysimeter captured A) phosphate (PO_4^{3-}) fluxes B) ammonium (NH_4^+) fluxes and C) total dissolved nitrogen (TDN) fluxes, D) ammonium to total dissolved nitrogen ratio (NH4/TDN), and E) Dissolved organic nitrogen (DON) from soil organic horizons in mature forest and harvested treatments. Values are means of 12 lysimeters per treatment. Asterisks indicate significant differences between treatments determined by repeated measures two-way ANOVA and post-hoc least-square means tests, alpha = 0.05. Grey bars indicate soil drying periods characterized by 10 or more consecutive days receiving less than 10 mm of rainfall. Boxplots show the median and confidence intervals of plot scale annual means (n=3 per plot type) of each solute (A-E).

Table 3.3: Pearson correlations between lysimeter captured dissolved organic matter (concentrations, ratios and fluxes) and environmental variables (soil temperature, moisture and water input) within mature forest (F) and harvested (H) treatments. Dissolved organic carbon (DOC), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), ammonium (NH_4^+), and orthophosphate (PO_4^{3-}). Bold font highlights significant correlations. A Bonferroni correction was applied to account for Type 1 Error (alpha = 0.05/3 = 0.017).



			A. soil temperature		B. soil moisture		C. water input	
		df	F	H	F	H	F	H
Concentrations	[DOC] mg C L^{-1}	23	r= 0.9493 t= 7.7154 **p< 0.0001**	r= 0.8083 t= 6.5847 **p<0.0001**	r= -0.2383 t= -1.177 p= 0.2512	r= -0.4773 t= -2.6052 **p= 0.01582**	r= -0.4325 t= -2.3008 p= 0.0308	r= -0.5431 t= -3.1022 **p= 0.0050**
	[TDN] mg N L^{-1}	21	r= 0.7708 t= 5.5451 **p<0.0001**	r= 0.7038 t= 4.5409 **p= 0.0001**	r= 0.0727 t= 0.3340 p=0.7412	r= -0.1563 t= -0.7253 p = 0.8305	r= -0.5010 t= -2.6529 **p= 0.0148**	r= -0.5398 t= -2.9388 **p= 0.0078**
	[DON] mg N L^{-1}	20	r= 0.2390 t= 1.1001 p= 0.284	r= 0.6749 t= 4.088 **p= 0.0006**	r= 0.2203 t= 1.010 p= 0.3245	r= -0.0864 t= -0.3880 p= 0.7021	r= -0.0978 t= -0.4398 p= 0.6648	r= -0.5242 t= -2.7531 **p= 0.0123**
	[NH_4^+] mg N L^{-1}	21	r= 0.6835 t= 0.7038 **p= 0.0003**	r= 0.7357 t=4.2911 **p<0.0001**	r= 0.01914 t= 0.08775 p= 0.9309	r= -0.3721 t= -1.8375 p= 0.0803	r= -0.6081 t= -3.5102 **p= 0.0021**	r= -0.5170 t= -2.7677 **p= 0.0115**
	[PO_4^{3-}] mg P L^{-1}	21	r= 0.6309 t= 3.7269 **p= 0.0012**	r=0.6592 t= 4.017 **p=0.0006**	r= -0.4021 t= -2.0123 p= 0.0572	r=-0.2287 t=-1.077 p=0.2939	r= -0.3933 t= -1.9604 p= 0.0633	r= -0.2904 t= -1.3912 p= 0.1787
Ratios	DOC:DON	20	r= 0.3279 t= 1.55 p= 0.1362	r= 0.1750 t= 0.79 p= 0.436	r= -0.5644 t= -3.0578 **p= 0.00621**	r= -0.5079 t= -2.6372 **p= 0.0158**	r= -0.068 t= -0.3066 p= 0.7623	r= -0.068 t=-0.3077 p= 0.7623
	NH_4^+:TDN	20	r= 0.4556 t= 2.2891 p= 0.0331	r= 0.2945 t= 1.3781 p= 0.1834	r= -0.2863 t= -1.3365 p= 0.1964	r= -0.4676 t= -2.366 p= 0.0282	r= -0.44 t= -2.194 p= 0.0402	r= -0.30 t= -1.4273 p= 0.1689
Fluxes	g DOC $m^{-2} d^{-1}$	28	r= -0.1387 t= -0.7412 p= 0.4647	r= -0.1575 t= -0.8437 p= 0.4060	r= -0.1282 t= -0.6843 p= 0.4994	r= -0.1454 t= -0.7779 p= 0.4431	r= 0.7358 t= 5.7500 **p<0.0001**	r= 0.6113 t= 4.0880 **p= 0.0003**
	g TDN $m^{-2} d^{-1}$	26	r= -0.3371 t= -1.8258 p= 0.0793	r= -0.2691 t= -1.4252 p= 0.1660	r= 0.01418 t= 0.0723 p= 0.9429	r= -0.0802 t= -0.4102 p= 0.6850	r= 0.8243 t= 7.1343 **p<0.0001**	r= 0.6610 t= 4.4925 **p= 0.0001**
	g DON $m^{-2} d^{-1}$	24	r= -0.3917 t= -2.0858 p= 0.0478	r= -0.3127 t= -1.6130 p= 0.1198	r= 0.0625 t= 0.3069 p= 0.7615	r= -0.0134 t= -0.0659 p= 0.9480	r = 0.7374 t= 5.2356 **p<0.0001**	r= 0.6627 t= 4.3356 **p= 0.0002**
	g NH_4^+ $m^{-2} d^{-1}$	26	r= 0.0528 t= 0.2700 p= 0.7892	r= 0.1340 t= 0.6899 p= 0.2251	r= -0.0829 t= -0.4242 p= 0.6749	r= -0.2031 t= -1.0582 p= 0.2997	r= 0.5101 t= 3.0239 **p= 0.0056**	r= 0.3769 t= 2.0753 p= 0.0479
	g PO_4^{3-} $m^{-2} d^{-1}$	26	r= 0.0232 t= 0.1187 p= 0.9064	r= 0.2367 t= 1.2426 p= 0.4209	r= -0.2663 t= -1.4090 p= 0.1707	r= -0.1855 t= -0.9627 p= 0.3445	r= 0.5771 t= 3.6033 **p= 0.0013**	r= 0.2916 t= 1.5545 p= 0.1322

Table 3.4: Repeated measures ANOVA results assessing the effect of treatment, collection day and their interaction on specific UV absorbance 254nm (SUVA), low molecular weight spectral slope (LMW), high molecular weight spectral slope (HMW), iron concentrations ([Fe]), aluminum concentrations ([Al]), the ratio of dissolved organic carbon to iron (DOC:Fe) and the ratio of dissolved organic carbon to aluminum (DOC:Al).



A. SUVA	DF	F-value	p-value
Treatment	1	10.858	**0.0033**
Date	6	44.715	**<0.0001**
Treatment:Date	6	2.138	0.0539

B. LMW	DF	F-value	p-value
Treatment	1	1.67	0.2099
Date	6	18.81	**<0.0001**
Treatment:Date	6	5.09	**0.0001**

C. HMW	DF	F-value	p-value
Treatment	1	2.81	0.1077
Date	6	18.12	**<0.0001**
Treatment:Date	6	3.33	**0.0045**

D. SR	DF	F-value	p-value
Treatment	1	0.05	0.8238
Date	6	31.9	**<0.0001**
Treatment:Date	6	1.51	0.1797

E. [Fe]	DF	F-value	p-value
Treatment	1	5.16154	**0.0332**
Date	6	26.1303	**<0.0001**
Treatment:Date	6	1.34221	0.2439

F. [Al]	DF	F-value	p-value
Treatment	1	4.09043	0.0554
Date	6	19.13497	**<0.0001**
Treatment:Date	6	0.89863	0.4984

G. DOC:Fe	DF	F-value	p-value
Treatment	1	3.38677	0.0793
Date	6	6.81007	**<0.0001**
Treatment:Date	6	1.05731	0.3922

H. DOC:Al	DF	F-value	p-value
Treatment	1	5.81735	**0.0247**
Date	6	1.96941	0.0754
Treatment:Date	6	0.56551	0.757

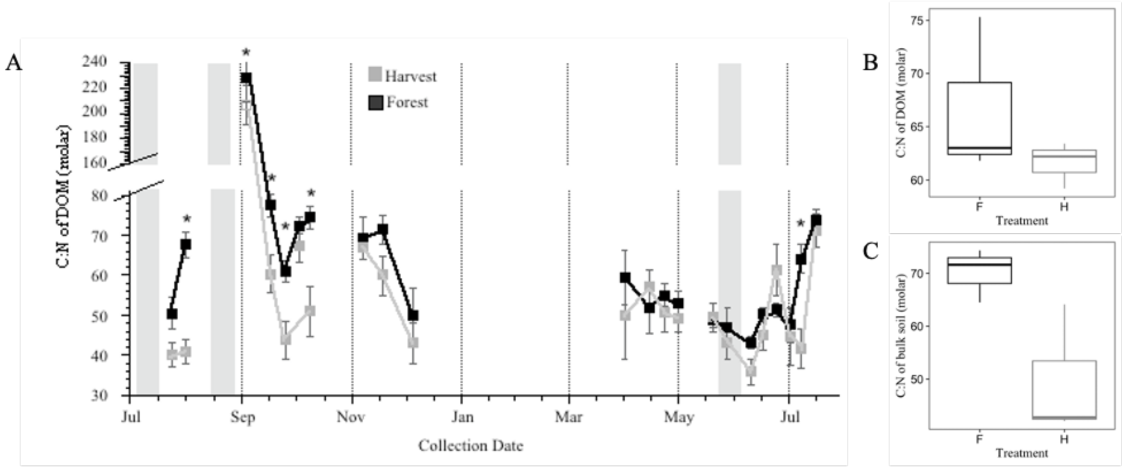


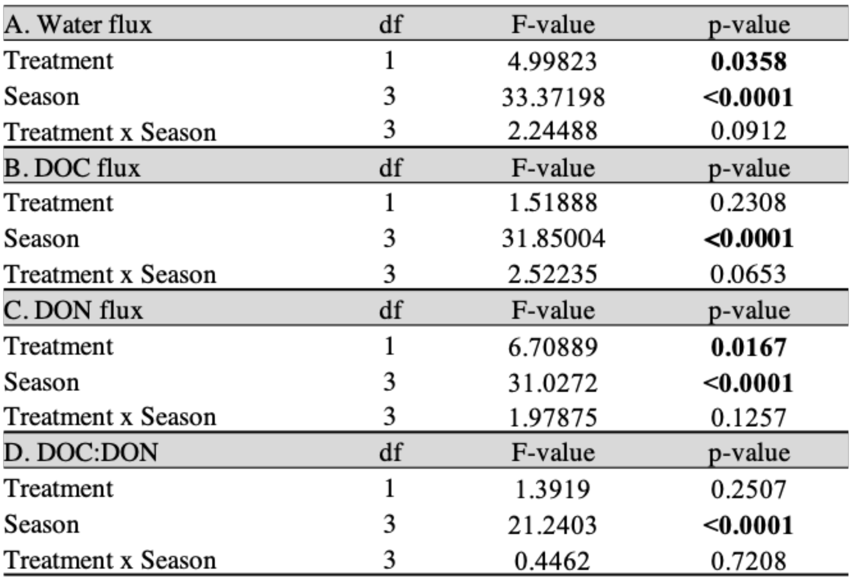
Figure 3.2: (A) Intra-annual variation of the dissolved organic carbon (DOC) to dissolved organic nitrogen (DON) ratio collected by lysimeters. Each point is a mean of 12 lysimeters per treatment per collections day. Grey bars designate periods of 10 consecutive days receiving less than 10 mm/day of precipitation. Breaks in the line graphs between points indicate periods of time when a sampling attempt was made but no water was captured by the lysimeters, indicating a zero flux. Asterisks indicate collection days where significant differences between treatments occurred as determined by a repeated measures ANOVA and post hoc least square means test, alpha = 0.05. (B) Boxplot of C:N of DOM in harvest(H) and forests(F) compared to (C) organic horizon C:N in H and F. Boxplots show the median and confidence intervals of plot scale annual means (n=3 per plot type).

3.3.3 Seasonal fluxes and concentrations in harvested and forest plots

An effect of season ($p<0.0001$) and treatment ($p = 0.0358$) was observed on total soil water fluxes with no interactive effect (Table 3.5). Soil water fluxes were always greater through the O horizons of H compared to F and the four seasonal periods (summer, autumn, winter and snowmelt/spring; see *Seasonal Designations* in methods) exhibited four different cumulative water flux periods (Figure 3.3A). The largest cumulative water fluxes in H and F occurred over the snowmelt period and the smallest water fluxes occurred during the winter when a consistent snowpack resulted in very low inputs of water to the soil. The second largest flux of water occurred during autumn, the only seasonal period when water fluxes were significantly different between treatments. A relatively small cumulative water flux occurred during the summer period, though still larger than the overwinter flux. All DOM fluxes exhibited an effect of season (Table 3.5; $p<0.0001$), but an effect of treatment was only observed for DON flux ($p = 0.0167$). No interactive effect of season and treatment on DOM fluxes was observed.

The largest total flux of DOC (Figure 3.3B) occurred during the autumn, and intermediate fluxes of DOC occurred in the summer and during snowmelt, which were not significantly different. The smallest total flux of DOC occurred during the winter. The largest total fluxes of DON occurred during both autumn and snowmelt periods. An intermediate flux of DON occurred during the summer, and the smallest flux occurred during the winter (Figure 3.3C). The relative seasonal DOC and DON patterns described above resulted in C:N of DOM that was highest in the summer, decreased in autumn, and was lowest during winter and snowmelt (Figure 3.3D).

Table 3.5: Repeated measures ANOVA results assessing the effect of treatment, season and their interaction on the total O horizon flux of water, dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and the ratio between DOC/DON. Seasonal variations of water flux, DOC flux, DON flux and DOC:DON are shown in Figure 3.3



A. Water flux	df	F-value	p-value
Treatment	1	4.99823	**0.0358**
Season	3	33.37198	**<0.0001**
Treatment x Season	3	2.24488	0.0912
B. DOC flux	df	F-value	p-value
Treatment	1	1.51888	0.2308
Season	3	31.85004	**<0.0001**
Treatment x Season	3	2.52235	0.0653
C. DON flux	df	F-value	p-value
Treatment	1	6.70889	**0.0167**
Season	3	31.0272	**<0.0001**
Treatment x Season	3	1.97875	0.1257
D. DOC:DON	df	F-value	p-value
Treatment	1	1.3919	0.2507
Season	3	21.2403	**<0.0001**
Treatment x Season	3	0.4462	0.7208

A principal component analysis (PCA) including absorbance properties (SUVA$_{254nm}$, SS$_{275\text{-}295nm}$, SS$_{350\text{-}395nm}$, and Sr), the C:N of DOM and DOC:Fe grouped by treatment (Figure 3.4A) and season (Figure 3.4B) demonstrated the overriding effect of season compared to harvesting. PC1 and PC2 describe 43.1% and 26.6% of the dataset variability respectively. Seasonally, autumn is characterized by higher molecular weight and higher C:N of DOM, while winter and snowmelt samples are characterized by higher SUVA$_{254nm}$ and Sr. Harvested and forested samples were weakly separated by SUVA and DOC:Fe.

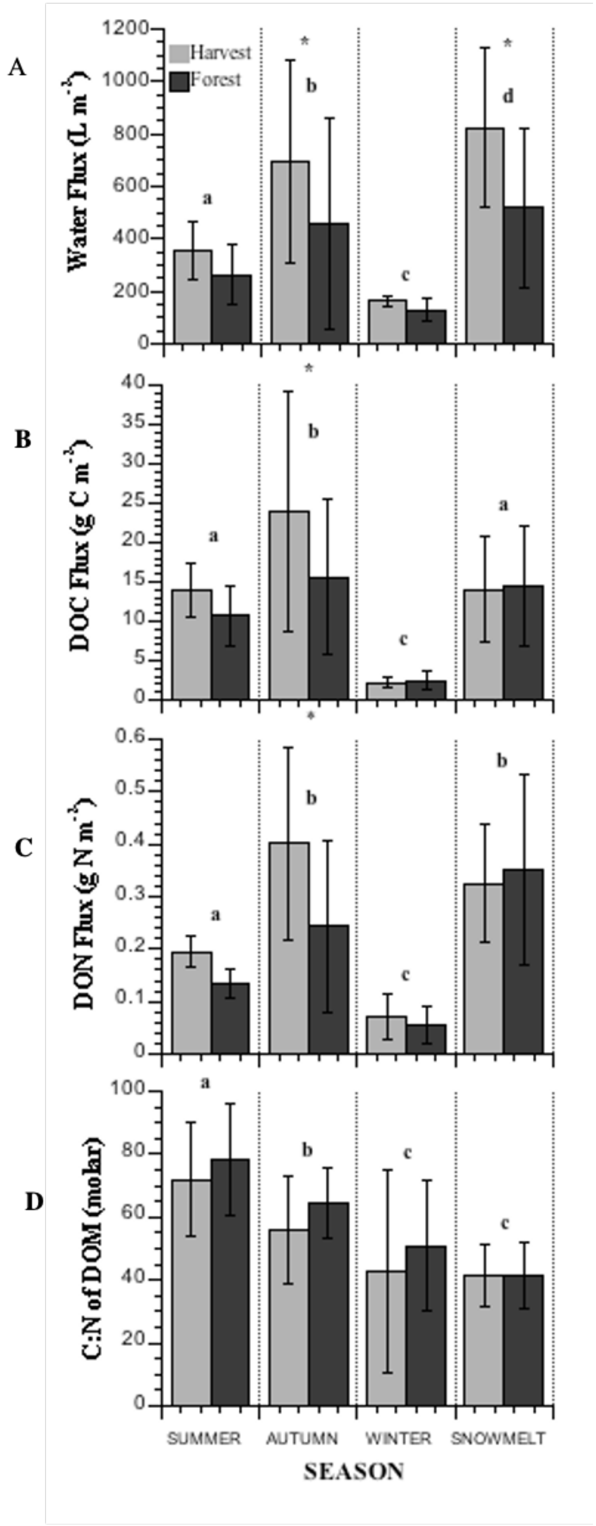


Figure 3.3: Total seasonal fluxes of water, dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and the C:N of DOM in the mature forest (F) and harvested (H) treatments. Seasonal designations are described in the methods section. Seasonal periods sharing the same letter are not significantly different. Asterisks indicate significant differences between treatments. Error bars show the standard deviation of 12 lysimeters per treatment per season.

3.4 Discussion

This study provides evidence for a strong control of season on the chemical composition of dissolved organic matter (DOM) mobilized from boreal forest organic (O) horizons that supersedes controls attributed to the long-term effect of forest harvesting. Clear cut harvesting reduces the interception of water immediately through the removal of trees but also through the longer-term reduction of the O horizon thickness and associated moss layer. Similar to dissolved organic carbon (DOC) fluxes (Bowering et al., 2020), this increased the mobilization of dissolved organic nitrogen (DON) on a weekly to annual scale. The relative temporal patterns of DOM composition, however, are similar in mature forest and harvested treatments. These patterns are indicative of mobilization of DOM of both fresh plant and microbial origin in the summer through autumn, and a shift to increased microbial biomass and microbially processed materials underneath a consistent snowpack during winter and the following snowmelt. These seasonal shifts highlight a potential sensitivity of DOM composition to the changing climate, particularly a changing snowpack regime, and support other studies describing the ubiquitous control of interacting soil ecological and hydrometeorological processes on the mobilization of DOM from soil among different forests within a similar climate region (Cronan and Aiken, 1985; Kaiser et al., 2001; Fröberg et al., 2011).

3.4.1 Summer soil DOM reflects decomposition of plant products and N mineralization

The high C:N and high molecular weight DOM mobilized in summer is explained by the dominance of the decomposition of fresh plant litter releasing water soluble organic C relative to organic N. Summer in this forested landscape is a period of relatively low precipitation, high soil temperature, and multi-day periods of soil drying followed by rewetting. Decomposition of litter resulting in the release of soluble materials at high soil temperatures (when moisture is not limiting), results in the release of soil C and

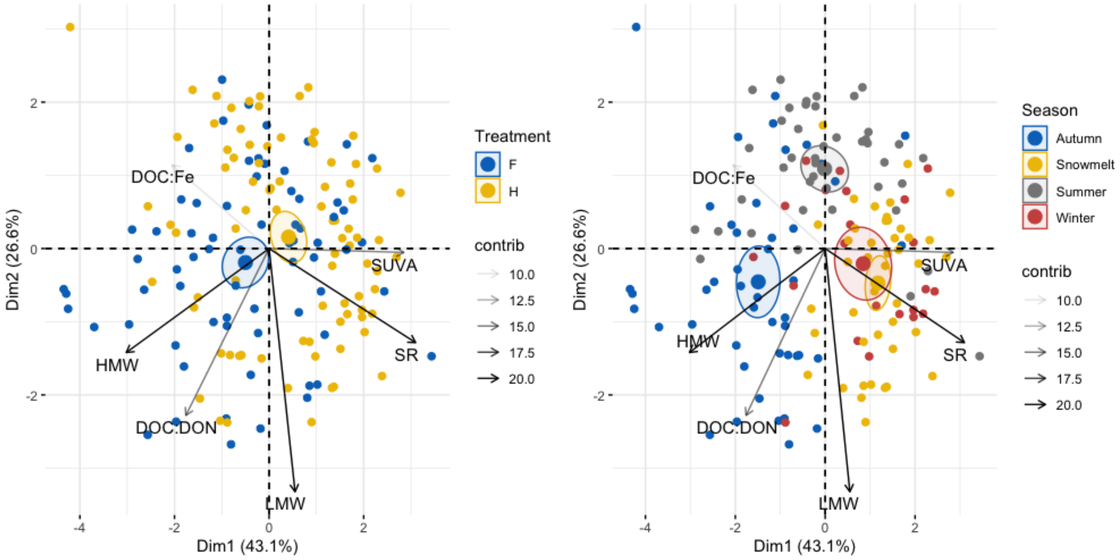


Figure 3.4: Principal component analysis biplots used to explore the predominant variables describing the harvesting effect compared to the seasonal effect on the composition of mobilized dissolved organic matter(DOM). Variables included are dissolved organic carbon (DOC) to iron ratio (DOC:Fe), the $SS_{350\text{-}395nm}$ indicative of high molecular weight (HMW) DOM, the $SS_{275\text{-}295nm}$ indicative of low molecular weight (LMW) DOM, the spectral slope ratio (Sr), specific ultraviolet absorbance (SUVA), and the C:N of DOM (DOC:DON). Treatments shown in A) include samples taken from the forest (F) and harvest (H) plots. Seasons shown in B) include samples taken from Autumn, Winter, Snowmelt and Summer. Vectors are shaded according to their combined contribution (contrib) to PCA1 and PCA2 (Dim1 and Dim2). Ellipses represent the 95% confidence interval around each group mean.

uptake or immobilization of N (Kirschbaum, 1995; Conant et al., 2011; Hilli et al., 2010). While greater proportions of C are mineralized and released as CO_2 during this period, a byproduct of greater microbial activity is greater production of soluble C, resulting in the high DOC concentrations and low pH often observed at high soil temperatures in laboratory extractions (Moore et al., 2008; Lee et al., 2018), and in situ (Kalbitz et al., 2007). Additional concurrent processes known to affect DOM production at high seasonal temperatures are soil drying and rewetting cycles (Fierer and Schimel, 2002), and rhizodeposition (Weintraub et al, 2007; Van Der Heijden et al., 2008). All of these processes could contribute to mobilized DOC in H and F plots in summer, although the later would contribute LMW DOM.

While the above processes result in an increase in DOC in summer, a number of other concurrent processes result in the transformation and uptake of dissolved ON. Higher rates of N mineralization likely contributed to the larger ratio of dissolved inorganic N (DIN) relative to total dissolved N (TDN) observed (Figure 3.1) and highlights the possibility of greater ON processing during summer. No detectable nitrate in soil leachates along with low pH of soil solution, suggests that nitrification in this system is limited (St. Marie and Pare, 1999). In addition, direct uptake of DON by vegetation during the growing season is possible in northern latitudes that are N deficient (Neff et al., 2003; Nasholm et al., 2009) with plants and microbes competing for low molecular weight DON, such as amino acids and peptides (Farrell et al., 2014). These processes limit the amount of ON available for mobilization during summer in H and F plots.

3.4.2 Autumn soil DOM indicates a progressive reduction in soluble C but maintenance of organic N

Following the relatively warm, dry summer period, the reduced temperature combined with increased plant inputs and decreased plant N demands in autumn lead to shifts in composition of mobilized DOM from H and F soil. Autumn, defined here as the period of continuous leaching of soil, constant soil moisture, and decreasing soil temperatures, resulted in initially high C:N of DOM, that decreased over the season. The sudden decrease in C:N of DOM observed at late autumn (Figure 3.2), suggests that the O horizon had been leached of much of the soluble organic C, while the available soluble organic N was maintained. Decomposition of litter and soil during summer in boreal coniferous forests is dominated by fungi, whose activity rely on seasonally dependent rhizodeposition (Žifčáková et al., 2017). Two important C inputs associated with the reduction of photosynthesis are therefore likely reduced in this system in late autumn: that from rhizodeposition and that from rhizo-dependent fungal decomposition of litter. In contrast to organic C trends, continued rapid cycling of organic N has been observed in northern black spruce forests of Alaska, even at low soil temperatures (Kielland et al., 2007) suggesting that continued breakdown of proteins replenishes the soluble ON pool during autumn. Furthermore, if DON uptake by plants is a relevant mechanism in this system, as is true in other northern systems (Schimel and Bennett; 2004), the demand for ON would decrease as plant activity slows in late autumn, reducing competition between the plant and microbial community for ON. This, in addition to decreasing rates of N mineralization with decreasing soil temperature contributes to the maintenance of the soluble ON pool compared to a decreasing soluble OC pool during the wet fall-to- winter transition.

3.4.3 Winter and snowmelt soil DOM reflect soil microbial contributions underneath the snowpack

Fluxes of low C:N, low molecular weight DOM occurring during winter and the following snowmelt period was likely the result of reduced plant inputs and maintenance of soil microbial activity underneath the snowpack. The winter period in this study year was characterized by a thick, consistent snowpack, that maintained constant soil temperatures at 2°C in both treatments. The snowpack developed before decreasing ambient temperatures could freeze the soil, allowing conditions for significant microbial activity underneath a consistently deep snowpack ($>$40 cm; Brooks et al., 2011). Soils under shallower snowpacks are more vulnerable to freeze-thaw events, resulting in fluctuations in microbial biomass through winter and periodic release of labile C (Schimel and Clein, 1996; Patel et al., 2018), such as carbohydrates and amino sugars (Kaiser et al., 2001). This can have significant impacts on growing season soil and stream DOC (Haei et al., 2010) and DON (Groffman et al., 2018) concentrations. In the absence of freeze-thaw cycles, cell lysis events may not be a significant mechanism of DOM release. Instead, microbial activity and decomposition of soil organic matter underneath the snowpack is likely the dominant source of DOM production over the duration of the winter. The low C:N, high $\text{SUVA}_{254\text{nm}}$ and high SR observed in winter and snowmelt samples, suggests the mobilization of relatively more aromatic, lower molecular weight DOM in comparison to summer and autumn. Although the higher SUVA in snowmelt DOM was initially surprising, these results support the occurrence of microbial degradation of soil organic matter in the absence of fresh litter inputs underneath the snowpack, which increases the solubility of large aromatic compounds such as lignin (Malcolm, 1990; Hansson et al., 2010; Klotzbücher et al., 2013).

3.4.4 Conclusions

This study demonstrates that the composition of mobilized soil DOM is similarly variable in two plot types with significantly different forest stand and soil structure. While clear-cut harvesting drives changes to forest water balance, through immediate removal of the canopy and longer-term reduction of the O horizon thickness, resulting in larger quantities of mobilized DOM, the response of soil DOM composition to season suggests that the mobilization of soluble materials in the two treatments are controlled by similar soil ecological and hydrometeorological mechanisms. This was first apparent through comparison of the C:N of DOM to C:N of the bulk soil. While C:N of DOM in F was similar, C:N of DOM in H was higher relative to the bulk soil. Optical properties and the C:N of DOM of samples collected during summer, autumn, winter, and snowmelt were reflective of shifts from plant-derived to microbial-derived DOM. The compositional shift observed during winter and snowmelt is especially noteworthy because temperature change at high-latitudes is expected to be more pronounced in the winter, with repercussions on snowpack formation and duration (Mellander et al., 2007; Laudon et al., 2013). Winter temperatures in this northern maritime climate often near 0°C, and a 7°C increase in mean winter temperature is projected for the end of the century (Finnis and Daraio, 2018). Future reductions in snowpack depth and duration as a result of increasing air temperature has the capacity to disrupt an important period of soil organic matter processing by microbes with repercussions on the composition of mobilized DOM during winter and snowmelt, however these effects are dependent on the type of snowpack change (Stark et al., 2020). In this eastern boreal region, snowpacks are deep (>80 cm maximum snow depth) and are likely to change in terms of the duration of the snow cover, increases in rain on snow events, and ice incasement, with soil freezing being a less significant concern in comparison to forests with shallower snowpacks (i.e. Groffman et al., 2018; Haei et al., 2013). Future work capturing variable snowpack years (either within or across sites) would help clarify the relative importance of these changes on the chemical character of soil organic matter and mobilized soil DOM, with implications on the fate of DOM within deeper mineral soils and the aquatic environment.

Chapter 4

Dissolved organic carbon mobilization across a climate transect of mesic boreal forests is explained by coupled air temperature and snowpack duration

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Abstract

The mobilization of soil dissolved organic carbon (DOC) is an important component of the terrestrial to aquatic (T-A) carbon flux. Controls on the T-A flux are difficult to define because of complex interactions between hydrological and biogeochemical processes operating at different temporal and spatial scales. In seasonally snow-covered environments, the snowpack holds both biogeochemical and hydrological significance as insulator of the soil during winter and reservoir of a large proportion of the annual precipitation that is released during spring melt. This four-year study was conducted within three maritime balsam fir forests spanning 47°N to 53°N. Mean annual precipitation (1074 mm to 1340 mm) and mean annual temperature (0°C to 5°C) decrease with increasing latitude. All three forests are consistently snow-covered throughout winter with snowpack depths sufficient to protect soils against freezing, however, there is a decrease in the amount of snowfall (462 to 393 cm), and a decrease in the length of the snowpack season (160 days to 109 days) from north (N) to south (S). Mean annual DOC mobilization increased from N to S but there was no relationship between annual DOC mobilization and annual precipitation, while there was a positive relationship with temperature at all sites. To interpret this result, a series of ecosystem-specific hydrometeorological indices were investigated, including those capturing productivity, precipitation event size and snowpack dynamics. Of the 16 models, air temperature and snowpack duration best described interannual and spatial DOC variability. Air temperature and snowpack duration were highly correlated, suggesting that air temperature indirectly affects DOC mobilization through a direct control on snowpack season length in these forests. Both warmer years and warmer sites have shorter snowpack seasons and mobilize more soil DOC, implying that these boreal forest soils are larger sources of C to mineral soil and/or aquatic networks under warmer conditions. Although the “colder soils in a warmer world” phenomenon is of concern in continental boreal forests experiencing increased occurrence of soil frost, observations from these maritime boreal forests are more likely explained by a combination of reduced winter heterotrophic soil C losses and increased soil water infiltration.

4.1 Introduction

The mobilization of soil dissolved organic carbon (DOC) is an important component of the terrestrial to aquatic (T-A) flux of the global carbon (C) cycle. Estimates of the global T-A flux have increased in magnitude through the last two editions of the International Panel on Climate Change (IPCC) report (Ciais et al., 2013; Denman et al., 2007) and, while small in comparison to global gross photosynthesis and respiration rates, the global T-A flux offsets estimates of global net land C sink (Webb et al., 2019). A greater mechanistic understanding of this flux is needed to refine estimates both globally and regionally and to enable accurate projections of T-A fluxes under future climate conditions. These estimates and projections are especially needed in high-latitude ecosystems which are warming faster than the global average (Hoegh-Guldberg et al., 2018), and contain approximately half of the global soil organic C pool (Hobbie et al., 2000; Tarnocai et al., 2009).

The mobilization of soil DOC is driven by biogeochemical and hydrological mechanisms but the relative dominance of these mechanisms and their interaction at different temporal and spatial scales is not clear (Jansen et al., 2014). A positive relationship between long-term precipitation (i.e., 30-year mean annual precipitation; MAP) and DOC fluxes at the continental scale (Michalzik et al., 2001) was confirmed at smaller spatial scales by some studies (Schmidt et al., 2010), but not by others (Borken et al., 2011; Fröberg et al., 2006; Lindroos et al., 2008). This suggests that a direct control of DOC fluxes by bulk precipitation is not ubiquitous. Many studies agree that soil water fluxes directly control DOC mobilization from O horizons (Tipping et al., 1999; Buckingham et al., 2008; Wu et al., 2014; Bowering et al., 2020), however, soil water fluxes can be decoupled from bulk precipitation inputs through canopy and forest floor interception, which is additionally affected by precipitation dynamics, such as intensity and type (Stan, 2020). Additionally, because long-term precipitation (i.e., MAP) is both a site condition influencing the vegetation type and a representation of water input, it may represent congruently operating direct and indirect controls on DOC mobilization that need to be disentangled.

The hydrology and C balance of boreal forests is strongly dependent on the structure and composition of the forest floor. Boreal forest transect studies in Alaska show that organic horizon depths increase from warmer sites to cooler sites, with implications for soil water storage (Kane and Vogel, 2009). Moss interception can be 23% of canopy interception (Price et al., 1997), and the latitudinal distribution of moss suggests that moss abundance is determined by temperature at large spatial scales (Berdugo et al., 2018). Therefore, the effect of increasing precipitation on DOC mobilization across boreal forest sites can be modulated by the proportion of precipitation that is intercepted by the forest floor - a factor dependent on the temperature sensitive thickness of the organic horizon and the abundance of moss cover.

Critically, a significant proportion of annual precipitation is received as snow in the boreal ecozone. In forests, the tree canopy intercepts more precipitation falling as snow rather than as rain (Starr and Ukonmaanaho, 2003). Therefore, the amount of water that reaches the forest floor is influenced by the interaction between canopy and precipitation type. Furthermore, significant processing of soil organic matter occurs underneath the snowpack of seasonally snow-covered environments (Brooks et al., 2011), which can affect the chemical character of DOC mobilized during snowmelt (Chapter 3). Colder soil temperatures and increased soil freezing are expected in snow-covered systems as warmer temperatures alter the amount and timing of snow accumulation resulting in “colder soils in a warmer world” (Groffman et al., 2001). Freezing increases DOC production in soils and increased DOC concentrations in streams (Haei et al., 2010). In addition, snowmelt is often the dominant hydrological event in seasonally snow-covered environments (Schelker et al., 2013), and has been shown to be a hot moment (Berhardt et al., 2017) of DOC export to streams (Finlay et al., 2006). Snowfall may still be sufficient to provide an insulative effect for soils in many forests in the current century, but increased variation in snowfall amount, timing of snowpack formation, snowpack depth, and increased frequency of mid-winter melting likely will result in meaningful consequences for soil processes and DOC mobilization.

To better understand the effects of temperature and precipitation on soil DOC mobilization in boreal forests at both annual and climatic scales, we conducted a study across sites experiencing different climates and collected data inter-annually for several years. Our objectives were to 1) evaluate the relationship between DOC mobilization and temporal and spatial variations in precipitation and temperature; and 2) evaluate the relative influences of interannual temperature, precipitation and hydrometerological indices on temporal variations in DOC mobilization relative to spatial variations. The hydrometeorological indices included are intended to capture variations in specific attributes of temperature, such as growing degree days, and specific attributes of precipitation, such as event size. Some indices capture interactions between temperature and precipitation, such as precipitation type and snowpack duration. In doing so, this study provides insights into the role of temperature and precipitation on DOC mobilization in maritime boreal forests, the response of soil DOC mobilization to future increases in temperature and precipitation, and the powerful influence of the timing of hydrologic fluxes on watershed-scale C transformations and movement.

4.2 Materials and Methods

4.2.1 Site Description

The study was conducted as part of the greater Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect (NLBELT) project taking place within three of four forested regions spanning 47°N to 53°N: Grand Codroy (GC), Salmon River (SR) and Eagle River (ER). The southern and intermediate regions (GC and SR) are located on the western portion of the island of Newfoundland, and the northern region (ER) is located in southeastern Labrador, Canada. Although three sites per region exist across NLBELT, only

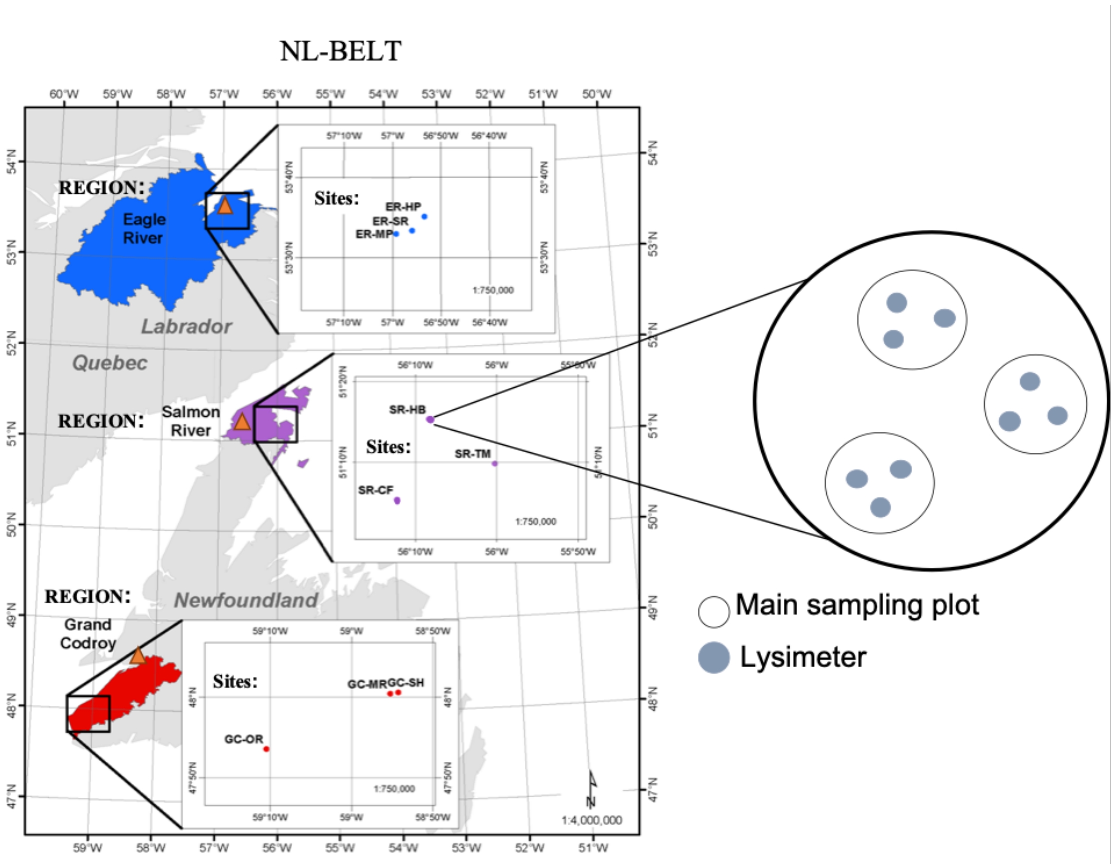
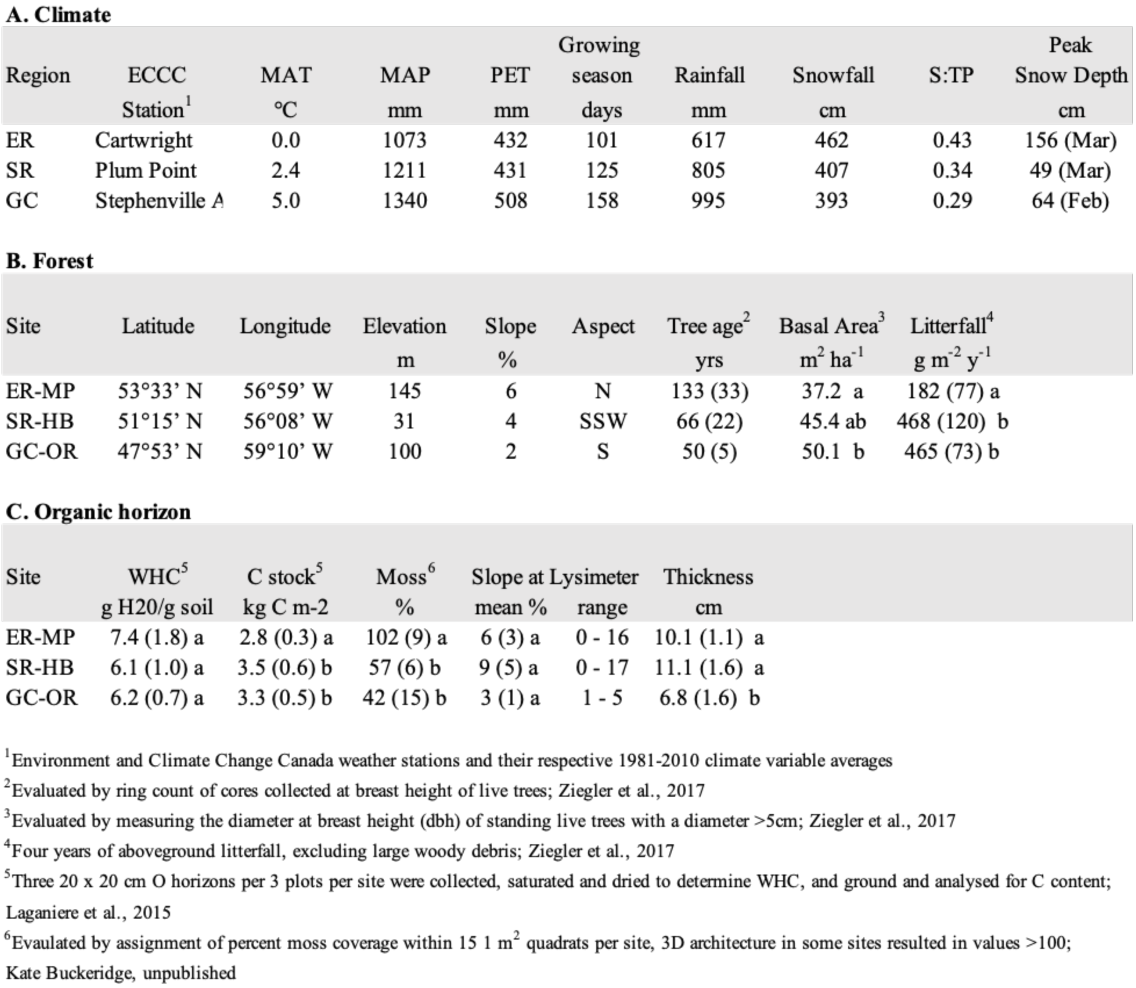


Figure 4.1: Three regions of the Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect that span 5 degrees latitude along the western coast of Newfoundland (Grand Codroy and Salmon River) and southeast coast of Labrador (Eagle River). Three balsam fir forest sites were established per region. Lysimeters were installed in one forest site per region (ER-MP, SR-HB and GC-OR). Three lysimeters (grey circles) were randomly distributed throughout three sampling plots per site. Climate data was retrieved from Environment and Climate Change Canada climate stations (orange triangles). Map is modified from Ziegler et al., 2017.

one site per region was selected for this study (ER- Muddy Pond, SR-Hare Bay, GC-O'Regans; Figure 4.1). Extreme wind events at the intermediate site (SR; data not shown) impacted litterfall during the study period.

Climate indices were derived from weather stations representative of each region (Environment and Climate Change Canada 30-year means, 1980-2010). Where there are multiple stations per region, the representative climate station was chosen based on the availability of precipitation data measured as both snowfall and rainfall. As a result, climate stations employed during this study differ from prior NLBELT studies (for example, Ziegler et al., 2017). Station information and climate data can be found in Table 4.1A.

Table 4.1: Climate, forest and organic horizon characteristics of the study sites. A) mean annual temperature (MAT), mean annual precipitation (MAP), growing degree days, rainfall, snowfall, and maximum snow depth are long-term climate normals 1981- 2010 provided by Environment and Climate Change stations stations representative of the three study regions (Eagle River (ER), Salmon River (SR), Grand Codroy(GC)). Month when maximum snow depth occurred is given in parentheses. b) The location, elevation, site slope, tree age, basal area, and aboveground litterfall at the three forest sites (ER-MP= Muddy Pond, SR-HB=Hare Bay, GC-OR= O'Regans) and c) The mean water holding capacity (WHC), carbon (C) stock, percent moss coverage, O horizon thickness and percent slope per forest site. Standard deviations of the mean are provided in parentheses. Lower case letters indicate significant site differences (alpha = 0.05)



A. Climate

Region	ECCC Station[1]	MAT °C	MAP mm	PET mm	Growing season days	Rainfall mm	Snowfall cm	S:TP	Peak Snow Depth cm
ER	Cartwright	0.0	1073	432	101	617	462	0.43	156 (Mar)
SR	Plum Point	2.4	1211	431	125	805	407	0.34	49 (Mar)
GC	Stephenville A	5.0	1340	508	158	995	393	0.29	64 (Feb)

B. Forest

Site	Latitude	Longitude	Elevation m	Slope %	Aspect	Tree age[2] yrs	Basal Area[3] m^2 ha^{-1}	Litterfall[4] g m^{-2} y^{-1}
ER-MP	53°33' N	56°59' W	145	6	N	133 (33)	37.2 a	182 (77) a
SR-HB	51°15' N	56°08' W	31	4	SSW	66 (22)	45.4 ab	468 (120) b
GC-OR	47°53' N	59°10' W	100	2	S	50 (5)	50.1 b	465 (73) b

C. Organic horizon

Site	WHC[5] g H20/g soil	C stock[5] kg C m-2	Moss[6] %	Slope at Lysimeter mean %	range	Thickness cm
ER-MP	7.4 (1.8) a	2.8 (0.3) a	102 (9) a	6 (3) a	0 - 16	10.1 (1.1) a
SR-HB	6.1 (1.0) a	3.5 (0.6) b	57 (6) b	9 (5) a	0 - 17	11.1 (1.6) a
GC-OR	6.2 (0.7) a	3.3 (0.5) b	42 (15) b	3 (1) a	1 - 5	6.8 (1.6) b

[1] Environment and Climate Change Canada weather stations and their respective 1981-2010 climate variable averages

[2] Evaluated by ring count of cores collected at breast height of live trees; Ziegler et al., 2017

[3] Evaluated by measuring the diameter at breast height (dbh) of standing live trees with a diameter >5cm; Ziegler et al., 2017

[4] Four years of aboveground litterfall, excluding large woody debris; Ziegler et al., 2017

[5] Three 20 x 20 cm O horizons per 3 plots per site were collected, saturated and dried to determine WHC, and ground and analysed for C content; Laganiere et al., 2015

[6] Evaulated by assignment of percent moss coverage within 15 1 m^2 quadrats per site, 3D architecture in some sites resulted in values >100; Kate Buckeridge, unpublished

Mean annual temperature (MAT) and mean annual precipitation (MAP) refer to the 30-year mean of annual temperature and precipitation at each site. There is an increase in mean annual precipitation (MAP; 1074 mm to 1340 mm) and an increase in mean annual temperature (MAT; 0°C to 5°C) with decreasing latitude, analogous to predicted climate change by the end of the century in Newfoundland and Labrador (Finnis and Daraio, 2018). All three regions are consistently snow-covered throughout winter. However, there is an increase in the amount of snowfall (393 to 462 cm), and an increase in the proportion of precipitation received as snowfall from south to north (0.29 to 0.43). Air temperature is consistently colder each month from S to N (Figure 4.2A), and that difference is enhanced during winter months (DJF; 7.2 difference between northern and southernmost sites) compared to summer months (JJA; 3.9 difference). Snowpacks develop earlier and melt later in the northern site and are generally deeper (ER maximum depth: 157 cm in March; Table 4.1A, Figure 4.2B). Total precipitation is evenly distributed throughout all months of the year with slightly drier conditions in all sites in March and April (for example, GC range 80 – 130 mm month^{-1}; Figure 4.2C).

All forest sites are dominated by balsam fir (*Abies balsamea*), with fewer black and white spruce (*Picea mariana* and *Picea glauca*). The southern and intermediate sites receive 60% more tree litterfall than the northern site, and have O horizons with a greater C stock, and less moss coverage. The northern and intermediate sites have thicker O horizons than the southern site. Detailed site characteristics of these sites are summarized in Table 4.1B,C.

4.2.2 DOC Flux measured in situ from Organic Horizons

Passive pan lysimeters were installed at the beginning of the 2011 growing season. Nine lysimeters were installed per forest site, with three distributed throughout three plots (Figure 4.1; ER-Muddy Pond, SR-Hare Bay, GC- O-Regan's). A 1 m^2 area was measured along the surface of the forest floor. The O horizon was cut and removed as a single, intact unit to permit installation of the lysimeters and then was returned to its original

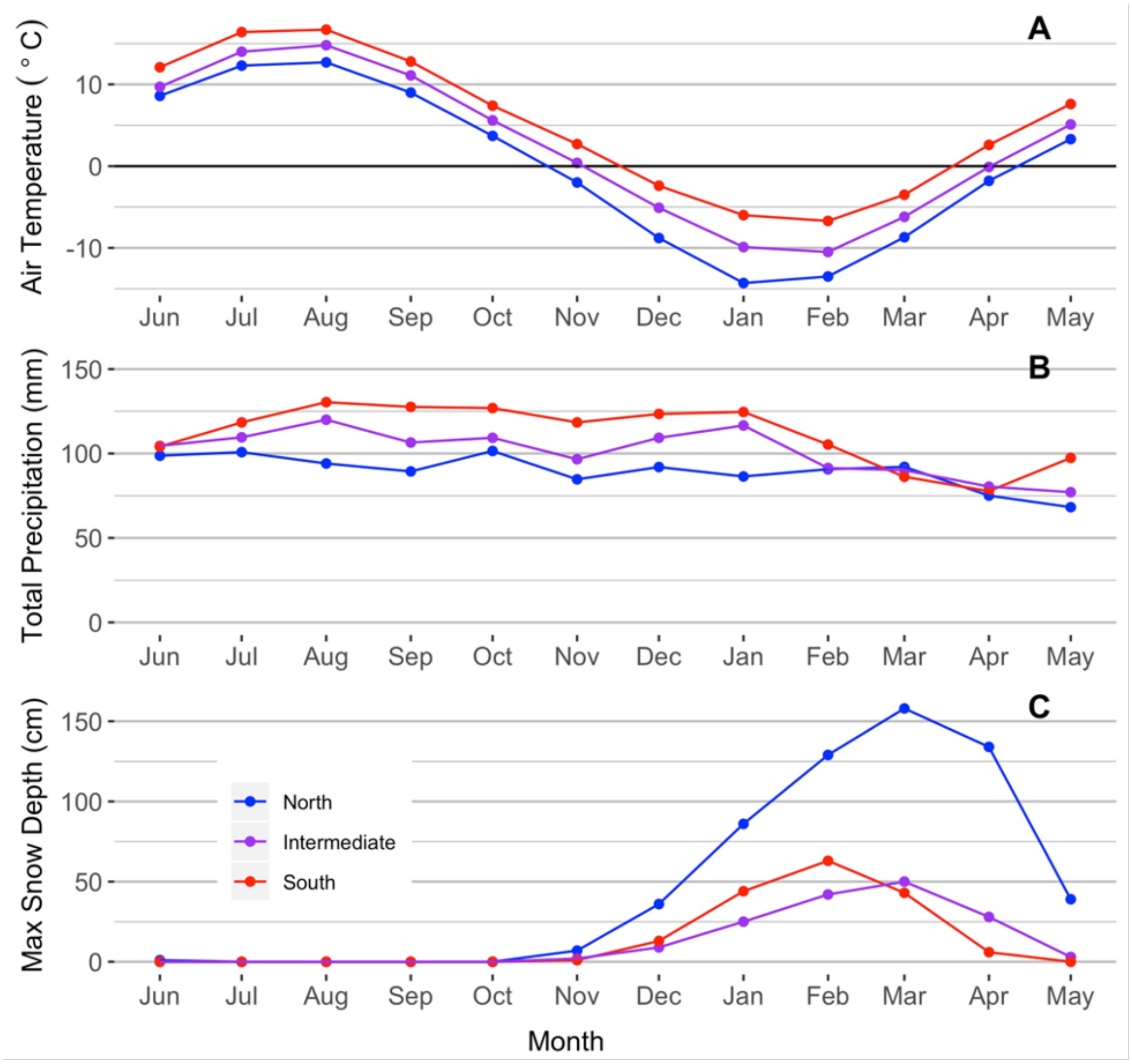


Figure 4.2: Regional comparison of 30 year mean monthly temperature, maximum snow depth, and total precipitation representative of three NLBELT sites. Data are derived from 1981- 2010 climate normals retrieved from Environment and Climate Change Canada Stations within each of the three regions: North (Eagle River) Intermediate (Salmon River) and South (Grand Codroy).

place. To determine the depth of the O horizon overlying each lysimeter, four depth measurements on each side of the removed O horizon were averaged (Table 4.1C). Slope (%) was determined along the length of each lysimeter (Table 4.1C).

The passive pan lysimeters consist of a 33.5 cm x 18 cm x 15 cm (length x width x depth) high density polyethelene "pan", overlain with a hard plastic screen to prevent large soil particles from entering the pan. Tubing connects the pan to an "overflow" container (10 L capacity) buried deeper in the mineral soil. Both receptacles have vertical cross-link polyethylene (PEX) tubing from the lowest corner to approximately 30 cm above ground, from which sample can be collected using a battery-operated pump. Maximum lysimeter capacity (catcher plus overflow) is approximately 14 L. Actual maximum volumes ranged from 12 to 14 L due to topographic heterogeneities that affected the installation of each pan and overflow within the landscape.

Lysimeter samples were collected over a four-year period from June 2011- June 2015 at least three times per year to capture relevant seasonal periods of autumn (plant senescence to snowpack formation), winter (persistent snowpack), and summer (plant growing season). Three of the nine lysimeters from each site received mercuric chloride through direct addition to the lysimeter pan after each sampling to reduce microbial processing of DOC between sampling dates. The effects of this were tested to determine the degree of sample transformation due to the long periods (up to several months) between collections, and were found to be insignificant; this practise was therefore stopped after 2 years of collections. Additionally, some lysimeters were damaged by moose and fallen trees during the first years of the experiment, so sampling effort was reduced to only 6 of the 9 lysimeters per site in years three and four. The 6 lysimeters captured the spatial variation of soil water and DOC fluxes within each site. Each lysimeter sample was filtered (Whatman GF/F) within two days of sampling and filtrate was immediately frozen. Samples were later thawed prior to analysis and DOC content was determined by high temperature combustion analysis (Schimadzu TOC-V). No effect of freeze/thaw on DOC loss via flocculation was observed.

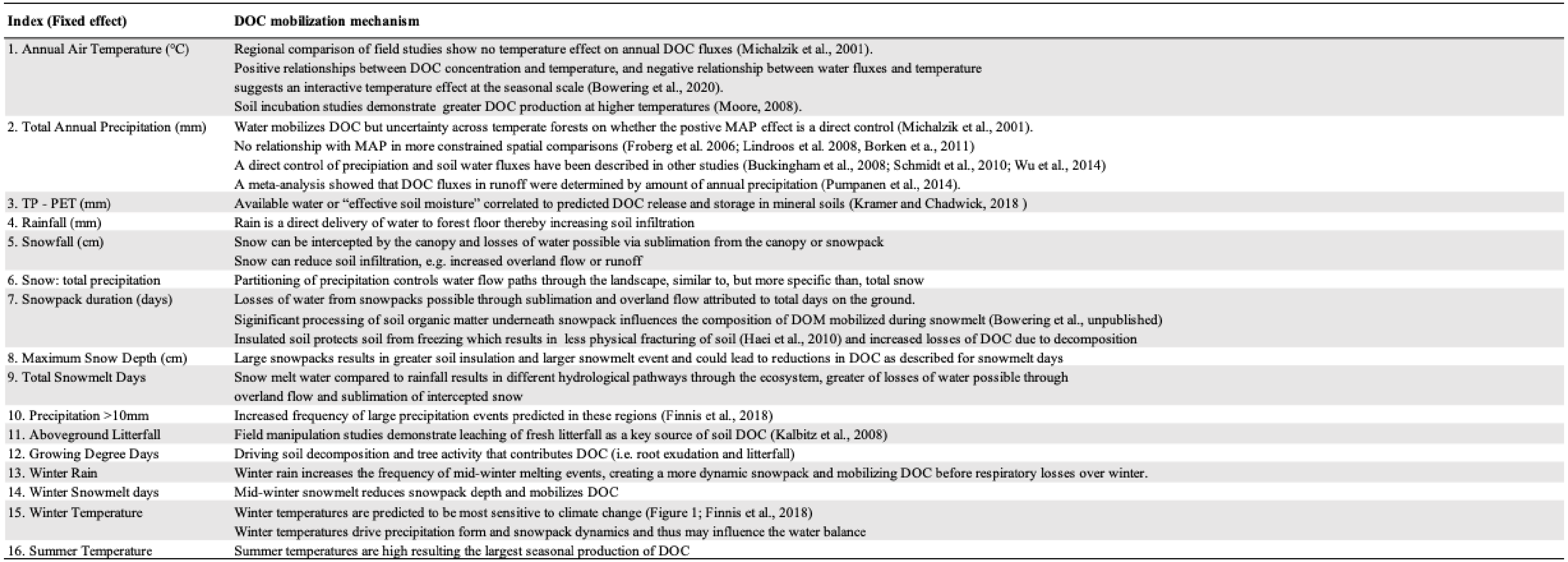
A DOC flux for a given collection period was the product of collected sample volume and measured DOC concentration over the catcher collection area, normalized to the number of collection days. On two occasions in summer 2012 the lysimeters in GC were emptied and volumes measured but sample was not analyzed for DOC content due to sampling constraints. For these collections, substitute [DOC] values were used from samples of the same lysimeters that were collected during a similar time of year, length of collection period, and collection volume. Estimates of annual DOC flux were determined for each site based on collections between summer 2011 and spring 2015. The 4-year mean annual fluxes were determined by averaging the time-adjusted (365 days) sum of the DOC flux collected over approximately annual periods (range 353 -393 days).

4.2.3 Statistical Analysis

All analyses were performed using RStudio Version 1.2.5019. Site differences in forest and O horizon properties were assessed using one-way ANOVAs (Table 4.1B,C). The relationship between DOC flux variability and four year interannual temperature and precipitation was assessed using repeated measures: linear mixed effects (rm-lme) models using the ‘car’ (Fox et al., 2020) and ‘nlme’ (Pinheiro et al., 2020) packages with forest site set as the random effect. Additional hydrometeorological indices likely to be affected by climate change were developed from the available data to reflect annual variations in precipitation form, snowpack formation and snowmelt dynamics and DOC production. These indices and associated DOC mechanisms are listed in Table 4.2.

A set of rm-lme models were designed from these indices with site included as the random effect in all. We note only one fixed effect parameter per model was included because of the small sample size (n = 4 years per site) and because many of the indices were correlated (Figure S1). All models were ranked by Akaike Information Criterion corrected for small sample size (AICc) using the ‘AICcmodavg’ package (Mazerolle, 2019). Top ranked models are models with ΔAICc = 0, calculated as the difference in AICc between the model and the focal model (model with the lowest AICc). Models with ΔAICc<2

Table 4.2: Hydrometeorological indices and DOC mobilization hypotheses. Annual temperature, total precipitation, total precipitation minus potential evapotranspiration (TP-PET), snowfall, rainfall, snowfall as a proportion of total precipitation (snow:precipitation), number of days with snow on the ground (snowpack days), maximum snowpack depth, snowmelt days (number of days above 0°C when snow is on the ground), precipitation ¿ 10mm (number of days receiving more than 10mm of precipitation. aboveground litterfall, and GDD (cumulative growing degree days >5°C), mean winter temperature, and total winter rainfall



Index (Fixed effect)	DOC mobilization mechanism
1. Annual Air Temperature (°C)	Regional comparison of field studies show no temperature effect on annual DOC fluxes (Michalzik et al., 2001). Positive relationships between DOC concentration and temperature, and negative relationship between water fluxes and temperature suggests an interactive temperature effect at the seasonal scale (Bowering et al., 2020). Soil incubation studies demonstrate greater DOC production at higher temperatures (Moore, 2008).
2. Total Annual Precipitation (mm)	Water mobilizes DOC but uncertainty across temperate forests on whether the postive MAP effect is a direct control (Michalzik et al., 2001). No relationship with MAP in more constrained spatial comparisons (Froberg et al. 2006; Lindroos et al. 2008, Borken et a., 2011) A direct control of precipiation and soil water fluxes have been described in other studies (Buckingham et al., 2008; Schmidt et al., 2010; Wu et al., 2014) A meta-analysis showed that DOC fluxes in runoff were determined by amount of annual precipitation (Pumpanen et al., 2014).
3. TP - PET (mm)	Available water or "effective soil moisture" correlated to predicted DOC release and storage in mineral soils (Kramer and Chadwick, 2018)
4. Rainfall (mm)	Rain is a direct delivery of water to forest floor thereby increasing soil infiltration
5. Snowfall (cm)	Snow can be intercepted by the canopy and losses of water possible via sublimation from the canopy or snowpack Snow can reduce soil infiltration, e.g. increased overland flow or runoff
6. Snow: total precipitation	Partitioning of precipitation controls water flow paths through the landscape, similar to, but more specific than, total snow
7. Snowpack duration (days)	Losses of water from snowpacks possible through sublimation and overland flow attributed to total days on the ground. Siginificant processing of soil organic matter underneath snowpack influences the composition of DOM mobilized during snowmelt (Bowering et al., unpublished) Insulated soil protects soil from freezing which results in less physical fracturing of soil (Haei et al., 2010) and increased losses of DOC due to decomposition
8. Maximum Snow Depth (cm)	Large snowpacks results in greater soil insulation and larger snowmelt event and could lead to reductions in DOC as described for snowmelt days
9. Total Snowmelt Days	Snow melt water compared to rainfall results in different hydrological pathways through the ecosystem, greater of losses of water possible through overland flow and sublimation of intercepted snow
10. Precipitation >10mm	Increased frequency of large precipitation events predicted in these regions (Finnis et al., 2018)
11. Aboveground Litterfall	Field manipulation studies demonstrate leaching of fresh litterfall as a key source of soil DOC (Kalbitz et al., 2008)
12. Growing Degree Days	Driving soil decomposition and tree activity that contributes DOC (i.e. root exudation and litterfall)
13. Winter Rain	Winter rain increases the frequency of mid-winter melting events, creating a more dynamic snowpack and mobilizing DOC before respiratory losses over winter.
14. Winter Snowmelt days	Mid-winter snowmelt reduces snowpack depth and mobilizes DOC
15. Winter Temperature	Winter temperatures are predicted to be most sensitive to climate change (Figure 1; Finnis et al., 2018) Winter temperatures drive precipitation form and snowpack dynamics and thus may influence the water balance
16. Summer Temperature	Summer temperatures are high resulting the largest seasonal production of DOC

are considered equally supported or not differentiable from the top-ranked model. The null hypothesis was included as the “site-only” model which states that DOC flux variations are described by differences in forest site properties and that there is no effect of interannual (i.e., short-term) variations in climate on DOC flux. These forest site properties developed under different historical climate conditions across the transect and are therefore, in part, a representation of the indirect (long-term) effects of climate. Forest properties related to water movement and DOC production include organic horizon thickness, moss coverage, C stock, litterfall, tree basal area, and slope, all of which differed across the latitudinal transect (Table 4.1). The southern site is characterized by less moss coverage, gentler slopes, a thinner O horizon, and a greater O horizon C stock compared to the northern site. The intermediate site resembles the northern site in some respects and the southern site in others. For instance, moss coverage and litterfall is similar in SR and GC, while organic horizon depth is similar in SR and ER.

4.3 Results

4.3.1 Environmental variability over study period in comparison to 30-year means

Large interannual variability in snowfall and snowpack dynamics in all regions

All sites exhibited above average annual temperature and received approximately average annual precipitation during the 4-year study period, when compared to the 1981-2010 (30- year) mean (Table 4.1A and 4.3). Latitudinal variation in precipitation and temperature over the study period was similar to 30-year mean, with an approximate 5.6°C increase in annual temperature and an approximate 200 mm increase in annual precipitation from the northern to southernmost site. Mean winter and summer temperatures increased with decreasing latitude, however, winter temperatures were more variable than

Table 4.3: Four-year means of hydrometeorological indices and variability (sd: standard deviation, cv: coefficient of variation) in three NLBELT regions. North (Eagle River), Intermediate (Salmon River), and South (Grand Codroy).

Variable		**North**	**Intermediate**	**South**
Annual temperature	mean	0.4	3.1	6.0
	sd	1.7	1.1	1.3
	cv	26%	34%	21%
Annual precipitation (mm)	mean	1094	1256	1301
	sd	115	130	269
	cv	11%	10%	21%
TP - PET	mean	775	770	750
	sd	169	82	315
	cv	22%	11%	42%
Winter (DJF) Temperature	mean	-12.7	-7.8	-4.5
	sd	2.3	1.8	1.4
	cv	18%	23%	31%
Summer (JJA) temperature	mean	12.6	14.0	16.2
	sd	1.1	0.9	0.9
	cv	9%	6%	6%
Snow:Precipitation	mean	0.40	0.29	0.32
	sd	0.08	0.04	0.13
	cv	20%	14%	40%
Snowfall (cm)	mean	437	357	424
	sd	70	44	202
	cv	16%	12%	48%
Rainfall (mm)	mean	662	898	930
	sd	135	125	189
	cv	20%	14%	20%
Winter (DJF) rainfall	mean	22	70	112
	sd	21	17	17
	cv	99%	24%	15%
Number of days w Precipitation>10mm	mean	33	41	38
	sd	5	5	11
	cv	15%	13%	29%
Snowpack duration	mean	169	130	109
	sd	17	28	26
	cv	10%	22%	24%
Total number of snowmelt days	mean	29	23	28
	sd	9	3	5
	cv	31%	13%	18%
Winter (DJF) snowmelt days	mean	1.3	4.3	10.3
	sd	1.5	2.2	3.5
	cv	120%	52%	34%
Maximum snow depth (cm)	mean	202	75	167
	sd	77	35	90
	cv	38%	47%	54%
Litterfall	mean	182	469	465
	sd	77	120	73
	cv	42%	26%	16%
GDD	mean	944	1171	1595
	sd	165	125	376
	cv	17%	11%	24%

summer and annual temperatures at all sites (CV: 18-31%). Congruent with the 30-year means, there was a larger latitudinal range in 4-year mean winter temperatures compared to summer temperatures (8.3°C and 3.5°C temperature range in winter and summer respectively). Rainfall decreased with increasing latitude and was slightly above average in ER and SR, but slightly below average in GC. Snowfall was approximately average in ER and GC and was below average at SR. Snowfall at GC was above average and was comparable to mean snowfall received at ER, however large interannual variations in snowfall occurred in GC (CV = 48%). Similarly, maximum snowpack depth in GC was much greater than 30-year average and was comparable to ER depths. There was large interannual variability of maximum snowpack depth at all sites, which increased with decreasing latitude (CV: ER = 38%, SR = 47%, GC = 54%). Snowpack duration (number of days from the beginning of a consistent snowpack to end of the melt) decreased with decreasing latitude (from 169 to 109 days). The number of within-winter snow melt days increased with decreasing latitude as did the amount of winter rainfall, but the total number of snowmelt days (melt days within winter and during spring) was similar at the three sites. Growing degree days were above average at all sites and increased with decreasing latitude. No clear latitudinal trend in the number of days receiving more than 10 mm of precipitation, the snowfall to precipitation ratio, or effective soil moisture (total precipitation – potential evapotranspiration) was observed over the study period.

4.3.2 O horizon dissolved organic carbon mobilization

Temperature and precipitation effects differ with scale

Regional comparison of long-term trends along the latitudinal transect revealed greater annual mobilization of soil DOC in the southernmost site that is characterized by both highest MAT and MAP ($p<0.0001$; Figure 4.3). Less DOC was mobilized in the northern and intermediate sites. The amount of DOC mobilized in the intermediate and northernmost sites was not significantly different despite a 2.6°C difference in MAT and 130 mm

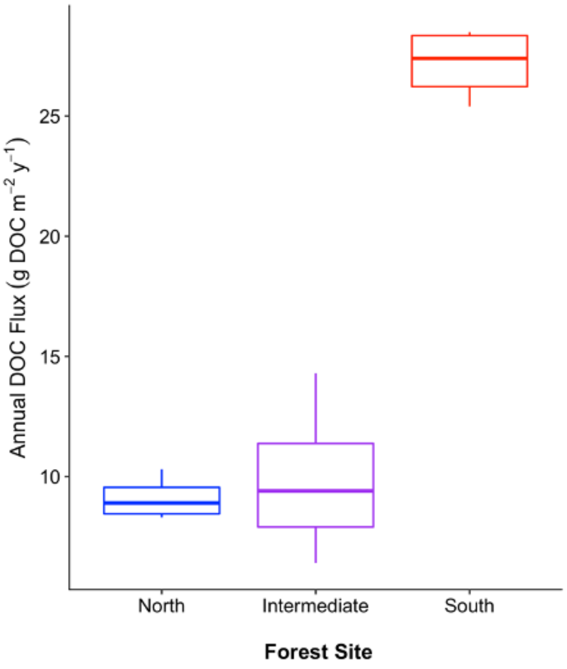


Figure 4.3: Boxplots of annual dissolved organic carbon (DOC) fluxes (g C m^{-2} y^{-1}) across a latitudinal transect. Sites are listed from North to South and increasing mean annual precipitation (MAP) and mean annual temperature (MAT). Box plots showing median and confidence intervals of four years of lysimeter captured annual DOC fluxes per site.

difference in MAP. There was no relationship between annual precipitation and DOC flux ($p = 0.8070$; Figure 4.4A). There was a positive relationship with annual temperature, with each one degree increase in MAT being associated with an increase in DOC flux of 8.31 g m^{-2} y^{-1} ($p = 0.0007$; Figure 4.4B).

Model selection indicates strong influence of air temperature and snowpack duration

Annual temperature, snowpack duration, effective soil moisture (TP-PET), snowfall and winter temperature were within 2 ΔAICc of one another and ranked above the null model (intercept + site effect; Table 4.4, Figure 4.5A). Indices related to total precipitation, rainfall, summer air temperature and productivity did not perform better than the null model. Annual air temperature explained 79% of the variance in DOC fluxes with ωAICc = 0.23. This model describes greater annual DOC mobilization at higher air temperatures. Winter temperature explained 74% of the DOC flux variance with ωAICc = 0.09. Similar

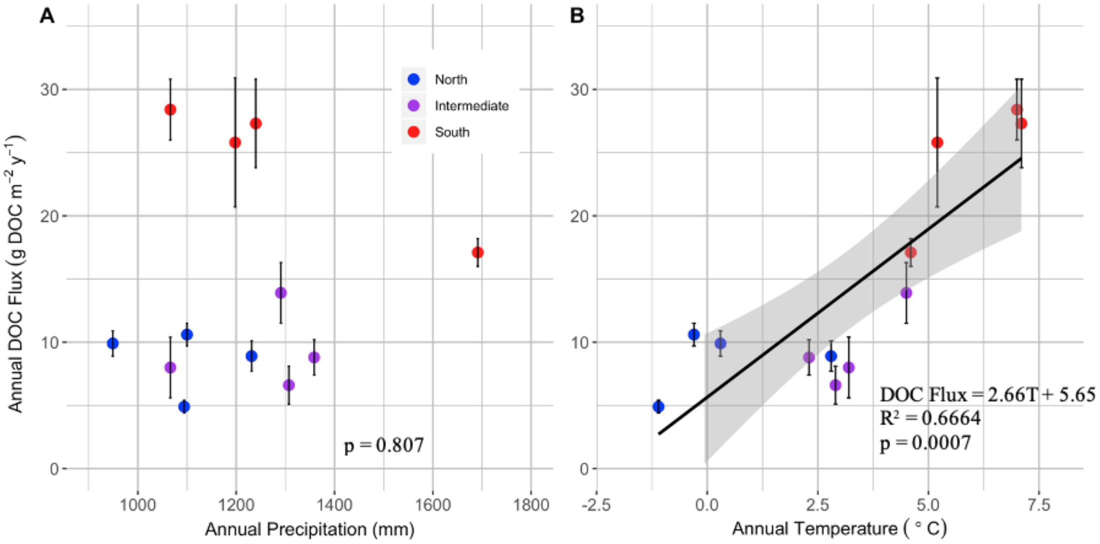


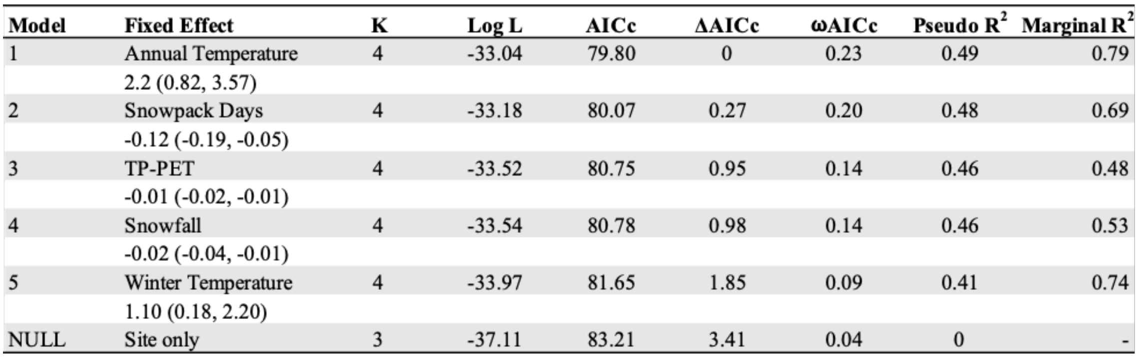
Figure 4.4: Relationships between DOC flux and (A) precipitation and (B) air temperature. The lysimeter captured dissolved organic carbon (DOC) fluxes measured over four years in southern (Grand Codroy; red), intermediate (Salmon River; purple), and northern (Eagle River; blue) forest sites. Error bars show standard deviation of the mean of all lysimeter collections per site per year. Trend line and 0.95 confidence interval (grey shading) demonstrates the significant linear relationship between DOC flux and air temperature.

to annual air temperature, more DOC is mobilized during warmer winters. The model including snowpack duration explained 69% of the DOC flux variance with ωAICc = 0.20, describing greater annual DOC mobilization during years with a shorter snowpack season. Air temperature and snowpack duration were highly negatively correlated (Figure 4.5B), suggesting that air temperature indirectly controls DOC mobilization through a direct effect on snowpack duration (i.e., warmer years result in a shorter snowpack season and more DOC mobilized). In contrast, total snowfall and effective soil moisture were not correlated to air temperature, and both parameters explained less of the DOC flux variance (48% and 53%, respectively).

4.4 Discussion

We found that, on average, more DOC is mobilized in the warmest, wettest region and less DOC is mobilized in the cooler, drier region of this boreal forest latitudinal transect.

Table 4.4: Results of model selection examining the interannual effect of air temperature, total precipitation, precipitation type (snowfall, rainfall, snowfall:precipitation) snowpack dynamics (snowpack duration, number of snowmelt days, maximum depth), precipitation event size (number of days exceeding 10mm total precipitation), productivity (growing degree days, litterfall), and winter dynamics (winter temperature, winter rainfall, winter snowmelt days). We included 16 linear mixed effects models in the model set, only those that ranked above the null are shown here. All models included site as the random effect. The null model includes the model intercept and random effects. Models are ranked with Akaike information criterion, corrected for small sample size. The fixed effects estimates and 0.95 confidence intervals (in parentheses) are included for the top ranked models.



Model	Fixed Effect	K	Log L	AICc	ΔAICc	ωAICc	Pseudo R^2	Marginal R^2
1	Annual Temperature	4	-33.04	79.80	0	0.23	0.49	0.79
	2.2 (0.82, 3.57)							
2	Snowpack Days	4	-33.18	80.07	0.27	0.20	0.48	0.69
	-0.12 (-0.19, -0.05)							
3	TP-PET	4	-33.52	80.75	0.95	0.14	0.46	0.48
	-0.01 (-0.02, -0.01)							
4	Snowfall	4	-33.54	80.78	0.98	0.14	0.46	0.53
	-0.02 (-0.04, -0.01)							
5	Winter Temperature	4	-33.97	81.65	1.85	0.09	0.41	0.74
	1.10 (0.18, 2.20)							
NULL	Site only	3	-37.11	83.21	3.41	0.04	0	-

These results suggest that climate change-driven increases in precipitation and temperature projected to occur in these mesic boreal forests by the end of this century will drive increased mobilization of soil DOC. Evidence from previous studies showing a positive relationship with precipitation and no relationship with temperature at the continental scale (Michalzik et al., 2001; Schmidt et al., 2010) suggest that increasing precipitation drives the climate transect trend observed here, and that temperature is not an influential factor. It was therefore surprising to find no relationship between annual bulk precipitation and DOC mobilization measured at our boreal forest sites (Figure 4.4A), but rather a positive relationship with annual air temperature (Figure 4.4B). By exploring additional hydrometerological factors over four years, we found that a significant part (69%) of the variation in DOC mobilization could be explained by snowpack duration which in turn is strongly influenced by variation in temperature (winter and annual; Figure 4.5B and Table 4.4). Furthermore, the remaining variability captured by other site attributes (i.e., the site factor in our models) suggests an additional influence of forest properties driven by long-term differences in climate at our sites. Organic horizon thickness and moss abundance

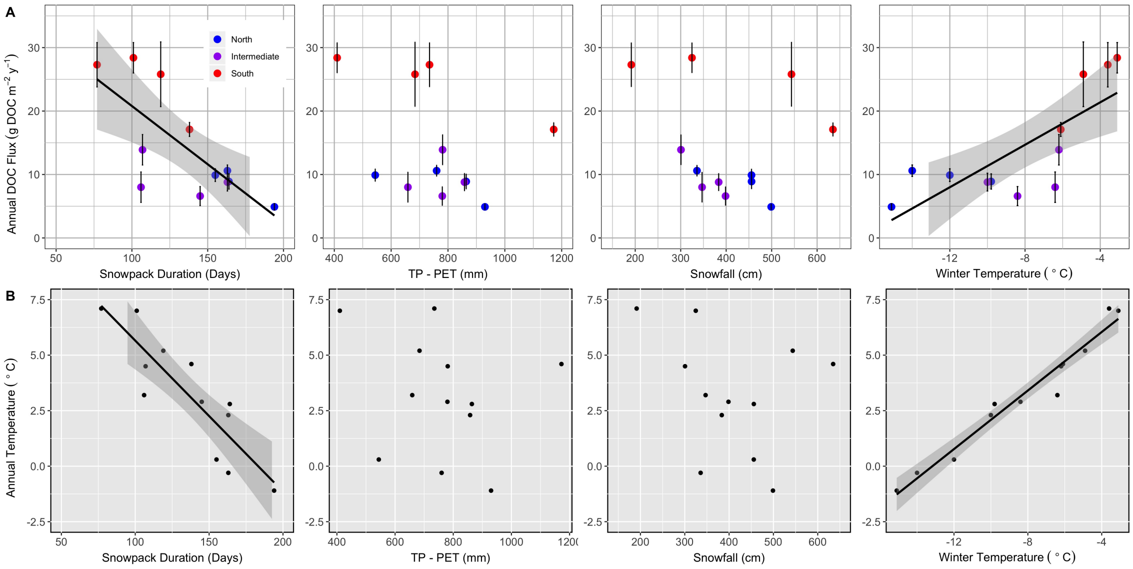


Figure 4.5: Plots of top models explaining dissolved organic carbon (DOC) flux variation by site selected by AICc (A), and top model factors plotted against annual air temperature (B). See Table 4.4 for parameter estimates (0.95 confidence intervals) and model selection results.

vary with latitude across the sites studied (Table 4.1C) and are important determinants of soil water storage and C accumulation in boreal forest soils (Hobbie et al., 2000; Kane and Vogel, 2009). Together, these results support a combined influence of both indirect, longer-term climate and short term hydrometeorological variation on DOC mobilization.

4.4.1 Temperature linked to snowpack dynamics explain short-term DOC mobilization dynamics

Even though many laboratory studies show that more DOC is extracted from soils incubated at higher temperatures (Christ and David, 1996; Lee et al., 2018; Moore et al., 2008), this effect has proven difficult to measure in field studies (Kalbitz et al., 2000). Weekly to biweekly DOC flux patterns usually resemble those of soil water fluxes, and not DOC concentration (Buckingham et al., 2008; Wu et al., 2014), supporting the hypothesis that hydrology, and not DOC production mechanisms, ultimately determine the quantity of DOC mobilized. This is what we predicted for these mesic boreal forest sites, thus the positive temperature effect and lack of precipitation effect observed here was unexpected. Temperature influences both forest productivity and water balance. The relative importance of these processes on DOC mobilization was seasonally-dependent in a mesic black spruce forest (Bowering et al., 2020) and congruent with seasonal patterns observed at the catchment scale (Wen et al., 2020). In this study, both annual and winter air temperature, together with snowpack duration and snowfall, ranked above production-related indices such as growing degree days and litterfall, highlighting the importance of the coupling of air temperature with hydrometerological characteristics in driving DOC fluxes in these mesic boreal forests.

Although we were unable to directly test this interaction, air temperature and snowpack duration were highly correlated (Figure 4.5B) and the effect of these two factors on DOC mobilization is likely linked. The timing and accumulation of the snowpack is highly sensitive to air temperature (Brooks et al., 2011). In many boreal regions, increased soil exposure during winter is expected to be a consequence of climate change, with resultant increases in DOC production and export from soils (Haei et al., 2010). In this study, all sites developed deep snowpacks early in the winter season that protected soils from freezing (>40 cm; Brooks and Williams, 1999). This suggests that the effect of varying snowpack duration is not explained by soil freezing in these sites. Two alternative explanations are consistent with our results: reduced winter heterotrophic soil C losses and increased soil water infiltration.

First, variations in the duration of the soil insulation period likely control DOC mobilization through length of the decomposition period. Soil respiration occurring underneath the snowpack can account for up to 50% of soil respiration in seasonally snow-covered systems (Brooks et al., 2011) and, as decomposition of organic matter proceeds in the absence of fresh litter inputs, the soluble fraction can decrease (Berg, 2000; Hilli et al., 2008). Consequently, less water-soluble organic C is available for mobilization during years with a longer snowpack season. In support of this, the chemical composition of DOC fluxes during snowmelt is measurably distinct from autumn, suggesting that snowpack has a direct influence on DOM composition and limits the quantity of soluble DOC released during snowmelt (Chapter 3).

Secondly, soil infiltration is impacted by both canopy interception and water flow paths during snowmelt. For instance, rain has greater leaching potential than snow because greater proportions of precipitation received as snow can be intercepted by the canopy and lost via sublimation resulting in decreased throughfall (Starr and Ukonmaanaho, 2003). The negative relationship between DOC mobilization and snowfall at all sites suggests a role of this process (Figure 4.5A), but with a strong site influence likely explained by decreasing stand density (Table 4.1B) and decreasing annual snowfall variability with increasing latitude (Table 4.3). Additionally, water movement within the snowpack can reduce the proportion of precipitation that infiltrates the soil and increase direct snowpack runoff. During large snowmelt events, within-snowpack water movement results in greater connection of the snowpack to the streams (Wever et al., 2014), and could in part explain why less soil DOC is mobilized during longer snowpack years.

4.4.2 Site properties are congruent with an influence of long-term climate on DOC mobilization

Differences in forest site properties across the transect suggests that long-term climate conditions explain additional DOC mobilization variability, indicating an indirect role of climate on DOC mobilization. The northern-most forests of this transect and the intermediate-latitude forests have thicker O horizons compared to the southern-most forests (Table 4.1C), which influences the interception potential of the forest floor. This could partly explain why the DOC fluxes in the south are consistently larger, even in years when total precipitation is equal across all sites (Figure 4.4A). Accumulation of C in organic horizons is ultimately determined by climate conditions controlling the balance between decomposition and inputs. On a global basis, low temperatures explain the accumulation of soil organic C in boreal forests compared to tropical forests. Within boreal forests, however, the driving mechanisms are not as clear (Ziegler et al., 2017), and are influenced by drainage class (Callesen et al., 2003; Olsson et al., 2009) and N deposition (Kleja et al., 2008), in addition to soil temperature (Kane et al., 2005; Kane and Vogel, 2009; Vogel et al., 2008). Moss abundance can also describe C accumulation trends in O horizons because of the relatively recalcitrant nature of moss litter compared to leaf litter (Hobbie et al., 2000; Philben et al., 2016). At large spatial scales, moss abundance increases with latitude (Berdugo et al., 2018), but within boreal forests, moss abundance is influenced by many factors including water availability and light (Brisbee et al., 2001), slope and aspect (Kane and Vogel, 2009), and deciduous litterfall (Jean et al., 2020). Similar to organic horizon interception, mosses can also influence large interception losses (Price et al., 1997). The northern forest site in the current study has significantly more moss coverage than the intermediate and southern sites, is north-facing, and receives significantly less litterfall than the forests in the other regions (Table 4.1B,C). Although the driving mechanisms behind these site factors require further investigation, differences in the structure of the organic horizon and associated moss layer are likely driven by long-term climate differences across the transect, with impacts on DOC mobilization through soil hydrological processes.

4.4.3 Conclusions and future directions

Climate change-driven increases in air temperature will have immediate consequences on snowpack duration and DOC mobilization patterns, but the longer-term response of the organic horizon (structure and composition) remain unclear. This study provides evidence for the indirect influence of both air temperature and longer-term ecosystem features on DOC mobilization from the O horizon, rather than the predicted direct control of bulk precipitation. While more DOC was mobilized, on average, in the wettest, warmest forest site, there was no relationship between DOC fluxes and annual precipitation when analyzed across all sites. In contrast, annual temperature appears to be positively linked to DOC fluxes. Multiple hypothesis testing of precipitation, temperature and additional hydrometeorological factors showed that air temperature and snowpack duration explained a large amount of DOC mobilization variability both interannually and spatially. Additionally, soil properties that developed under a small range of historical climate conditions may decouple DOC fluxes from annual precipitation, contributing to the strong site effect. Observations from boreal forest organic horizons studied here suggest more work is needed to understand the combined indirect and direct effects on DOC mobilization and the importance of each under rapidly changing environmental conditions. This will improve our ability to predict soil DOC mobilization and provide a better understanding of the contribution of soil DOC to aquatic C cycling.

Chapter 5

Summary

5.1 Summary and General Conclusions

Recent recognition of the pivotal role of soil dissolved organic matter (DOM) in linking terrestrial to aquatic systems (Roulet and Moore, 2006; Jansen et al., 2014) has directed interest in tracing DOM properties during mobilization through catchments (Van Gaelen et al., 2014; Araujo et al., 2016; Ni and Li, 2020), understanding the interaction between DOM dynamics and hydrological processes (Lohse et al., 2009; Klotzbrucher et al., 2014; Kellerman et al., 2014; Moravec and Jon Chorover, 2020), and identifying the major effects of various anthropogenic disturbances (Mattsson et al., 2005; Kreutzwiser et al., 2008; Xenopoulos et al., 2020). The organic horizon is a hydrologically and biogeochemically unique forest catchment unit, and a major source of DOM to downstream pools both within the soil profile and to aquatic systems. In boreal forests, organic horizons can be particularly thick and store a large proportion of the total soil C stock. In this dissertation I addressed questions related to the mobilization of boreal forest DOM from soil organic horizons at different spatiotemporal scales and discuss the relevance of these findings in the context of soil organic matter stability, catchment scale processes and climate change. Detailed information on soil DOM properties and mobilization dynamics is a prerequisite to tracing inputs of soil DOM in surface waters and identifying moments of mobilization that are most sensitive to climate change. Furthermore, soil DOM properties could potentially be used to understand the stability of soil organic matter, however, there is little confidence in a ubiquitous relationship between soil organic matter and soil DOM. Such relationships would enable the use of DOM as an indicator of soil condition and could be particularly useful at northern latitudes where surface soil C stores are large and vulnerable to rapid changes in air temperature.

A challenge of tackling these questions is capturing and parsing out the main effects of many processes that operate and interact at different temporal and spatial scales. Therefore, a unique aspect of my dissertation is the use of two mesic boreal forest research platforms that enabled investigation of DOM processes at numerous scales, from weekly to decadal and from plot to regional (Figure 5.1), and the use of both observational and laboratory techniques to address these questions. Figure 5.1 shows that at small temporal scales, water fluxes are the predominant driver of DOM dynamics, but as time scales increase from weekly to seasonal to annual, the effect of temperature becomes more apparent. At decadal scales the larger climate impact of temperature (MAT) and precipitation (MAP) was detected, likely indicative of the long term effect of climate on ecosystem properties such as the organic horizon thickness and moss coverage. Spatially, the effect of water flux also dominates smaller scales. However, in our plot-scale experiment at PBEWA, soil temperature and organic horizon thickness were also relevant to describing differences in DOM dynamics in harvested and forested plots. At regional spatial scales, I show the impact of snowpack duration linked to air temperature as well as the role of stand density, moss cover and O horizon that explained differences in soil hydrology, thereby indirectly driving DOM mobilization dynamics, as observed through comparison of sites along NLBELT. Altogether, an increased understanding of the relevance of DOM dynamics requires specific outlining of the scale of interest in order to identify the pertinent information required for addressing concerns, whether it be climate change, sustainable forestry practices, water quality, or soil carbon sequestration.

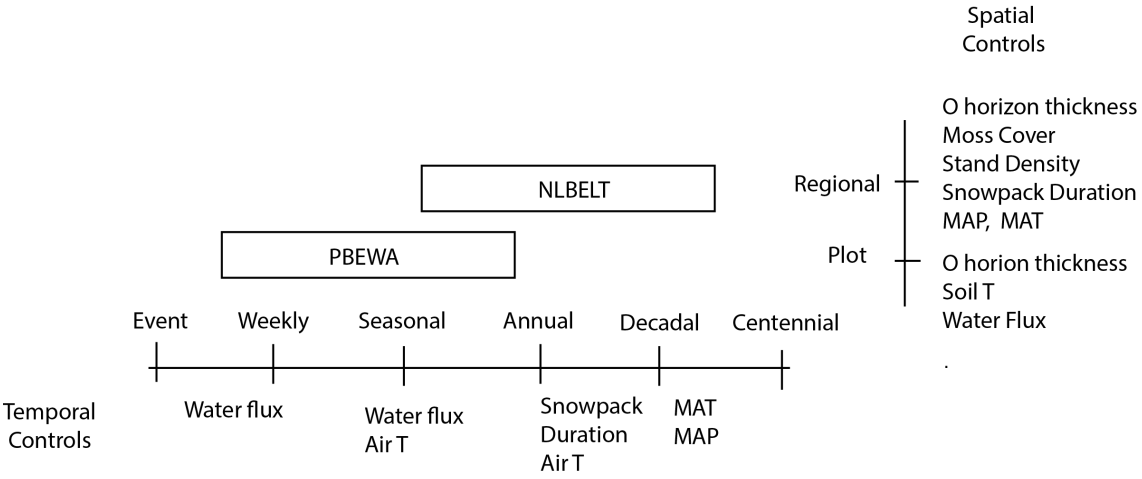


Figure 5.1: Dominant controls on dissolved organic matter (DOM) mobilization at different spatio-temporal scales in forests of the Pynn's Brook Experimental Watershed Area (PBEWA) and the Newfoundland and Labrador Boreal Ecosystems Latitudinal Transect (NLBELT). T= temperature, MAP= 30 year mean annual precipitation, MAT = 30 year mean annual temperature.

5.2 Outline of major findings

The major findings drawn from the three manuscript chapters of this dissertation are:

1) Water is the primary driver of the mobilization of DOM at the weekly to annual scale, but the relationship between DOM and water fluxes is seasonally variable and suggests an important secondary temperature control that results in water-limited and production-limited seasons. Summer and winter are periods of water limitation on DOM mobilization because of low water inputs to the soil, while autumn and snowmelt have a production-limitation on DOM mobilization because of large and rapid water inputs during low soil temperatures.

2) Lateral fluxes of water and DOM both within the organic horizon and across the interface of the organic and mineral horizons significantly reduce the magnitude of carbon and nutrients delivered to mineral soils under saturated conditions and rapid water flow. Modelling of porous, moss-covered organic horizon fluxes requires specific soil hydrological modelling efforts based on macropore flow dynamics and the specific hydraulic properties of living mosses and organic horizons, rather than models built on mineral soil characterization assumptions.

3) The composition of mobilized DOM from organic horizons is seasonally variable and is not significantly different in mature forest compared to 10-year post harvest plots. High C:N DOM, low SUVA (Specific Ultra Violet Absorbance), and low Sr (spectral slope ratio) occurs in the summer. While C:N of DOM decreases through autumn, winter and snowmelt, all optical parameters increase, which suggests a shift from fresh plant-based to microbial processing of soil organic matter. In addition to the composition of mobilized DOM, the rate of delivery of DOM to mineral soils varies seasonally.

4) The magnitude of DOC mobilized is sensitive to future changes in temperature and snowpack dynamics. Reductions in the duration of the snowpack due to increased winter temperature will result in increased mobilization of DOC from boreal forest organic horizons. Moss coverage and the thickness of organic horizon are also climatically influenced and play important soil hydrological and biogeochemical roles, indirectly affecting DOM mobilization, but it is unknown if the response of soil and understory vegetation to climate change will be as immediate as the direct (i.e., short-term) response of DOM mobilization to hydrometeorological changes.

5.3 Implications

The temporal and spatial patterns of soil DOM mobilized from O horizons in relation to key soil and meteorological parameters discussed throughout my dissertation contribute to 1) prediction of soil DOM mobilization under current and future climate conditions and 2) understanding the role of O horizon DOM dynamics in the context of catchment scale terrestrial to aquatic carbon and nutrient fluxes.

5.3.1 Climate and climate change

Currently, a typical year in western Newfoundland and Labrador (Figure 5.2) is one where total monthly precipitation is evenly distributed throughout the year with increasing pro-

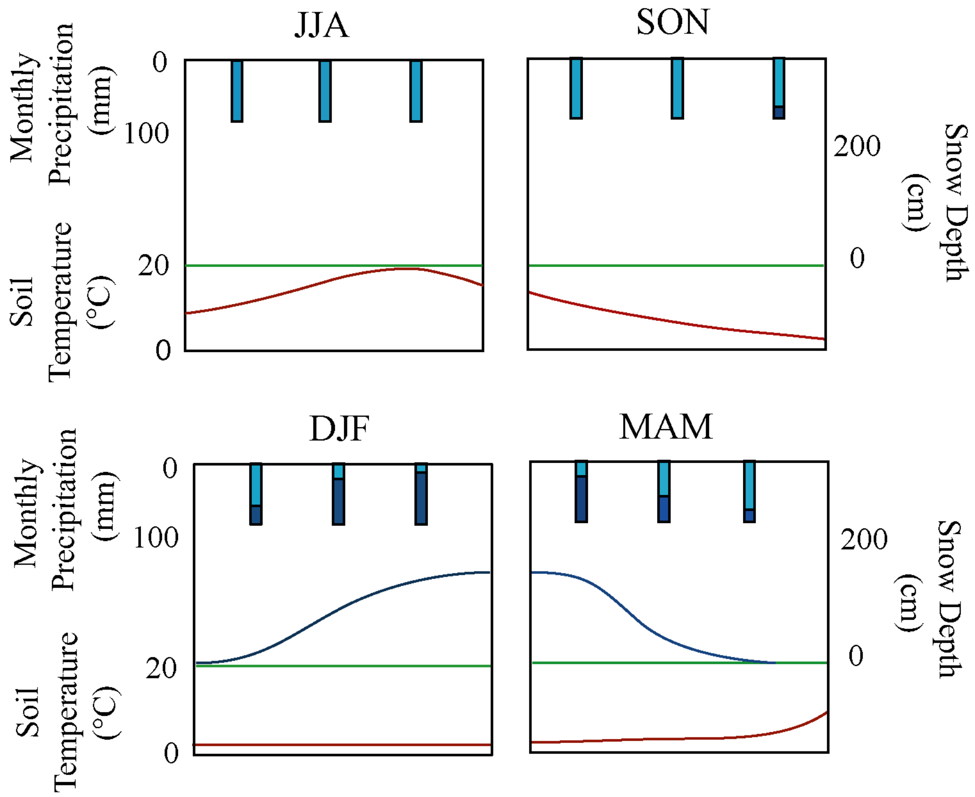


Figure 5.2: Seasonal trends in western Newfoundland and Labrador forests relevant to dissolved organic matter mobilization. Total monthly precipitation (blue vertical bars), monthly snowfall (dark blue inset of vertical bars), snow depth (blue continuous line, soil temperature (brown continuous line) and the forest floor (green line). Summer = JJA (June, July, August), Autumn = SON (September, October, November), Winter = DJF (December, January, February), Spring = MAM (March, April, May).

portions of snowfall in late autumn through winter. The snowpack begins to accumulate in early winter and increases in depth through winter to a maximum depth by early spring. Snowmelt rapidly occurs and depletes the snowpack before the end of the spring season. Soil temperature peaks in mid-summer, decreases through autumn and maintains a consistent above freezing temperature underneath the snowpack. Climate change projections for western Newfoundland and Labrador include increased frequency of large precipitation events, especially in autumn, resulting in increases in total annual precipitation, and increases in temperature in all seasons but more rapid increases in winter temperature (Finnis and Diario, 2018). These projections mean that the seasonal scenarios relevant to DOM mobilization (Figure 2) will also change.

I found that changes to the interactive dynamic between snowpack accumulation and soil temperature, and increased autumn rainfall and soil temperature are most likely to impact future DOM mobilization dynamics. The snowpack functions as both an insulator of the soil, protecting it from freezing at sub-zero atmospheric temperatures during winter, and a reservoir of the precipitation received over the winter period that is rapidly released during spring snowmelt. These attributes resulted in reduced mobilization of DOM with low C:N over the winter period and rapid mobilization of dilute, relatively low C:N, and low molecular weight DOM during spring snowmelt as observed in the Pynn's Brook Experimental Watershed (PBEWA), indicative of soil organic C processing underneath the snowpack and the contrasting winter and spring water flux dynamics. Additionally, greater mobilization of DOM occurred during warmer years and forest sites with shorter duration of the snowpack as observed in NLBELT forests. This suggests that future increases in winter air temperature in these areas will indirectly cause increased mobilization of DOM through changes to snowpack dynamics.

In contrast, results from PBEWA demonstrate a water-DOC flux relationship where water is the primary direct driver of DOM mobilization but decreasing temperature exerts a production limit on DOM mobilization during autumn and snowmelt. This suggests that increases in rainfall accompanied by increases in soil temperature will result in an alleviation of the production limitation (i.e., DOM no longer diluted by increased water fluxes), which in turn will lead to increased mobilization of DOM during the wet autumn and snowmelt periods.

5.3.2 Terrestrial to aquatic linkages

This dissertation provides information on both the hydrological and biogeochemical role of the boreal soil organic horizon important to terrestrial-aquatic (T-A) linkages. Organic horizons are both an important source of DOM and a significant influence on the water balance of the soil profile. First, lateral flow within the O horizon and associated moss layer, and along the interface between the O and mineral horizons, significantly affected the total DOM flux measured on over half of the sampling dates in PBEWA. Lateral flow predominately occurred during saturated, high flow periods in the PBEWA study. These results warrant the inclusion of lateral flow and explicit hydrological modelling of the porous moss + organic horizon in modelling efforts, such as what is being done in peatlands (Waddington et al., 2013). Secondly, the composition of mobilized DOM from organic horizons is seasonally variable and strongly impacted by snowpack dynamics. This has implications for the fate of soil DOM and how terrestrial DOM is identified in downstream pools because mobilized O horizon DOM does not have a steady state chemical signature. For instance, the increase in aromatic content and simultaneous decrease in C:N of samples collected in winter and snowmelt compared to summer and autumn signifies a consequence of soil microbial activity and shift toward increased microbial contributions to soil DOM. Thirdly, the findings regarding the significant influence of snowpack dynamics on DOM and water mobilization from organic horizons are in keeping with the influence of snowpack dynamics on streamflow in snow-covered systems, where snowmelt represents the major hydrological event of the year and is sensitive to changing climate, however, how snowpacks will change is spatially diverse with varying consequences on the underlying soil environment (Stark et al., 2020).

5.4 Future Directions

In order to better understand the fate of the soil DOM mobilization patterns and composition described in this dissertation in the context of soil organic matter stability, terrestrial to aquatic linkages and climate change, future studies should address the following questions:

1) In PBEWA, I identified significant lateral flow likely occurring both within the O horizon and along the interface with the mineral horizons along an approximately 8-12% hillslope under saturated, high water flow conditions. How significant is the lateral flow of water and DOM at the O to mineral horizon interface with respect to catchment scale

processes and connection of upland forest surface soil to the aquatic environment? Is this a more significant factor of soil DOM delivery to surface waters in sloped topographies compared to flatter landscapes (i.e.. refer to western versus eastern boreal in Figure 1.3).

2) In PBEWA, I showed that DOM mobilized during winter and snowmelt has a lower C:N, lower molecular weight, but higher relative aromatic content than DOM mobilized in summer and autumn. How does the interaction between O horizon DOM composition and rate of flow to and within mineral soil affect the capacity of minerals to adsorb and sequester DOM? This question could first be investigated through identifying the maximum carbon sequestration capacity of the mineral soils in PBEWA, as others have done (for example, Kalbitz and Kaiser, 2008). A second laboratory experiment that adjusts both the flow rate and composition of DOM delivery to minerals could help us understand the interaction between the two factors. A third step would be to apply and validate this laboratory information through seasonal field collections using passive lysimeters and pieziometers at different soil depths.

3) Using the NLBELT forest sites, I show that snowpack duration explains DOM mobilization dynamics both interannually and between sites. However, snowpacks interact with the soil both as an insulator and as a reservoir of precipitation. Therefore, does a reduced snowpack result in greater mobilization of DOM predominately through altering of the hydrological cycle (i.e., greater residence time and infiltration of water through O horizons) or to the biogeochemical cycle (i.e., reduction in over-winter insulation period and winter respiration)? Snowpack manipulation experiments are particularly helpful for understanding the effect of snowpacks on soil biogeochemistry conditions (i.e. Patel et al., 2018; Stark et al., 2020). Lysimeter collections made under similar snow manipulations could help get at the hydrological impacts of a changing snowpack in comparison.

4) The NLBELT forests exist within a constrained range of boreal climate conditions. Despite this, the forests of the southern sites differ significantly from the northern forest in terms of rates of C and N cycling (Philben et al., 2016; Ziegler et al., 2017), as well as the existing understory vegetation. The northern sites, for instance, are up to 100% moss cov-

ered, whereas the southern sites are on average less than 50% moss covered. The southern site represents an approximate 100-year change in climate conditions of the northern site, however, will the understory vegetation and organic horizon respond to the current rate of climate change and how relevant are those changes to DOM mobilization relative to the direct response of DOM mobilization to changes in hydrometeorological conditions, such as precipitation amount and type? Will increased DOM mobilization contribute to the future mass loss of the soil organic horizon? One way of moving this forward would be to better understand the controlling factors on moss growth in these forests. At the moment, it is not clear if the moss coverage variability is driven by water availability, light availability or nutrient availability differences across the NLBELT forests. Understanding the controls on moss distribution would help us to identify how quickly mosses are likely to respond to the rapid changes of environmental conditions in these boreal forest sites.

5) Together the information gained on DOM mobilization form PBEWA and NL-BELT forest sites are representative of mesic boreal forests with high precipitation, low PET, high annual rainfall and snowfall, and deep snowpacks. Are the driving factors of DOM mobilization and the significance of the upland forest O horizon applicable in forests across the topographically and climatically diverse boreal zone? For instance, moisture is not expected to limit temperature-driven increases in primary productivity in northeastern North America like it is in the western North America (D'orangeville et al., 2016). Will predictions of increased autumn DOM mobilization in these sites be relevant to moisture-limited sites? Repeating this experimental design in other forests of the boreal zone would help identify the factors that are ubiquitous across boreal forests, and those that are relevant to a dry boreal forest in comparison to the wet boreal forests described in this dissertation.

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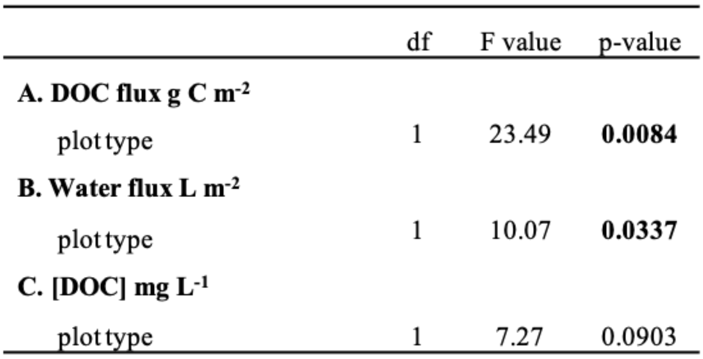
Appendix A

Supplementary Material

Table S1: Results of repeated measure linear mixed models assessing the effects of plot type, collection day and the interactive effect of collection day and plot type (forest and harvested) on temporal variations in lysimeter captured dissolved organic carbon (DOC) fluxes, water fluxes and DOC concentration. P-values shown with significant results in bold ($\alpha = 0.05$). Post hoc least squares means tests used to determine significant differences between plot type shown in Figure 1D-F (asterisks).

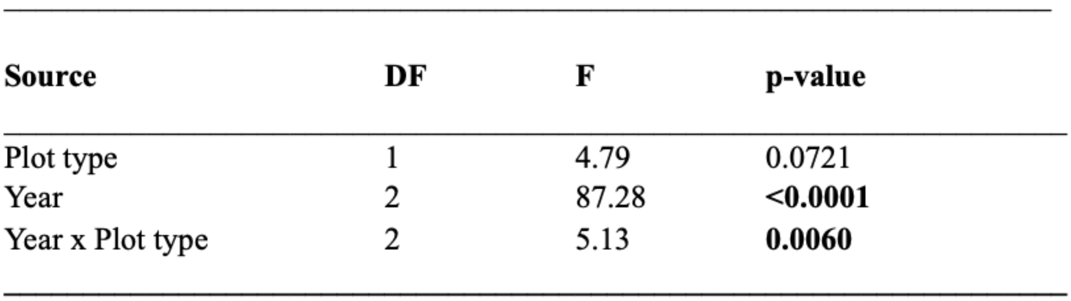
	df	F value	p-value
A. DOC flux g C m^{-2} d^{-1}			
plot type	1	3.88	0.0616
collection day	29	23.49	**<0.0001**
plot type x collection day	29	1.51	**0.0183**
B. Water flux L m^{-2} d^{-1}			
plot type	1	4.98	**0.0361**
collection day	29	26.71	**<0.0001**
plot type x collection day	29	2.36	**0.0004**
C. [DOC] mg L^{-1}			
plot type	1	7.27	**0.0132**
collection day	24	48.45	**<0.0001**
plot type x collection day	24	2.90	**<0.0001**

Table S2: Results of one way plot nested ANOVAs assessing the effects of plot type on annual lysimeter captured dissolved organic carbon (DOC) fluxes, water fluxes and DOC concentration. P-values shown with significant results in bold (α= 0.05). Plot type differences shown in Figure 2A-C (asterisks).



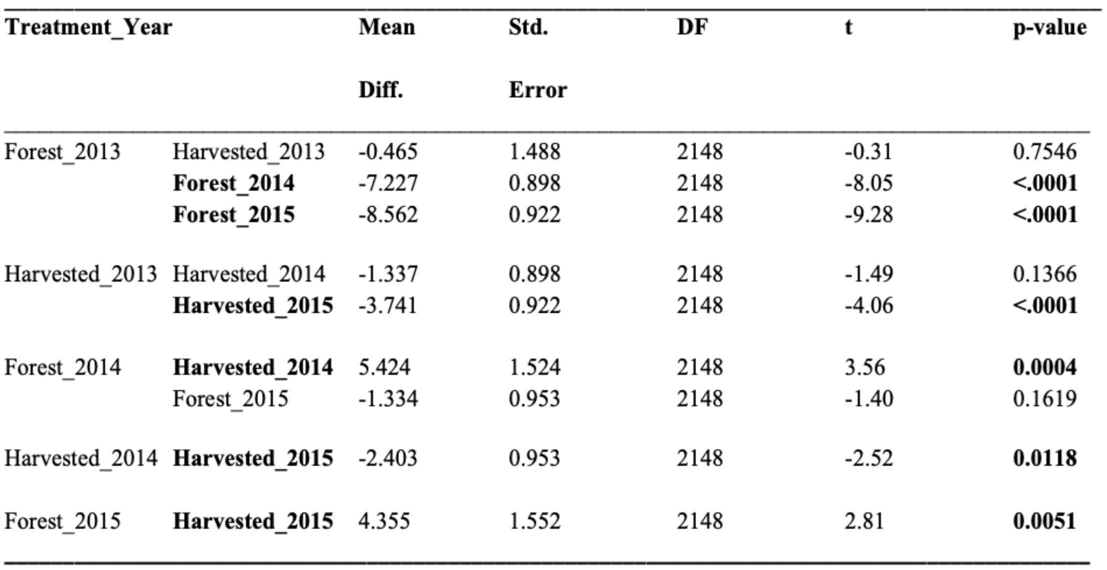
	df	F value	p-value
A. DOC flux g C m^{-2}			
plot type	1	23.49	**0.0084**
B. Water flux L m^{-2}			
plot type	1	10.07	**0.0337**
C. [DOC] mg L^{-1}			
plot type	1	7.27	0.0903

Table S3: Linear mixed effects model results examining the effects of plot type, sample year (2013, 2014, 2015), and their interaction on soil respiration. α= 0.05.



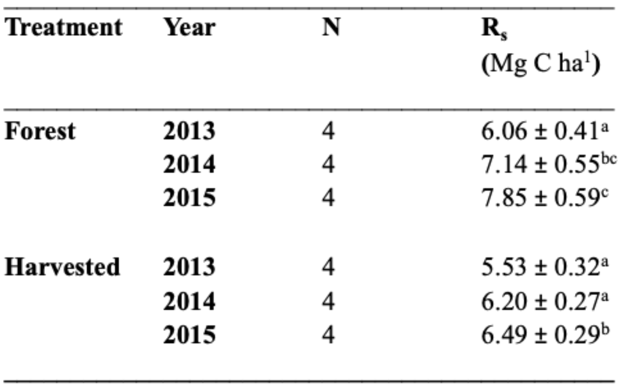
Source	**DF**	**F**	**p-value**
Plot type	1	4.79	0.0721
Year	2	87.28	**<0.0001**
Year x Plot type	2	5.13	**0.0060**

Table S4: Least square means for multiple comparisons of soil respiration (CO_2 m^{-2} s^{-1}) in black spruce forest across plot type (harvested and forest) and sample years (2013-2015). Soil respiration was measured during the snow-free growing season. α= 0.05.



Treatment_Year		**Mean Diff.**	**Std. Error**	**DF**	**t**	**p-value**
Forest_2013	Harvested_2013	-0.465	1.488	2148	-0.31	0.7546
	Forest_2014	-7.227	0.898	2148	-8.05	**<.0001**
	Forest_2015	-8.562	0.922	2148	-9.28	**<.0001**
Harvested_2013	Harvested_2014	-1.337	0.898	2148	-1.49	0.1366
	Harvested_2015	-3.741	0.922	2148	-4.06	**<.0001**
Forest_2014	**Harvested_2014**	5.424	1.524	2148	3.56	**0.0004**
	Forest_2015	-1.334	0.953	2148	-1.40	0.1619
Harvested_2014	**Harvested_2015**	-2.403	0.953	2148	-2.52	**0.0118**
Forest_2015	**Harvested_2015**	4.355	1.552	2148	2.81	**0.0051**

Table S5: Mean cumulative soil respiration for the snow-free growing season in four forest plots and four harvest plots. N refers to the number of plot-scale replicates. Values connected by the same letter are not significantly different as determined by lsmeans tests shown in Table S4).



Treatment	**Year**	**N**	**R_s (Mg C ha^{1})**
Forest	**2013**	4	6.06 ± 0.41^{a}
	2014	4	7.14 ± 0.55^{bc}
	2015	4	7.85 ± 0.59^{c}
Harvested	**2013**	4	5.53 ± 0.32^{a}
	2014	4	6.20 ± 0.27^{a}
	2015	4	6.49 ± 0.29^{b}

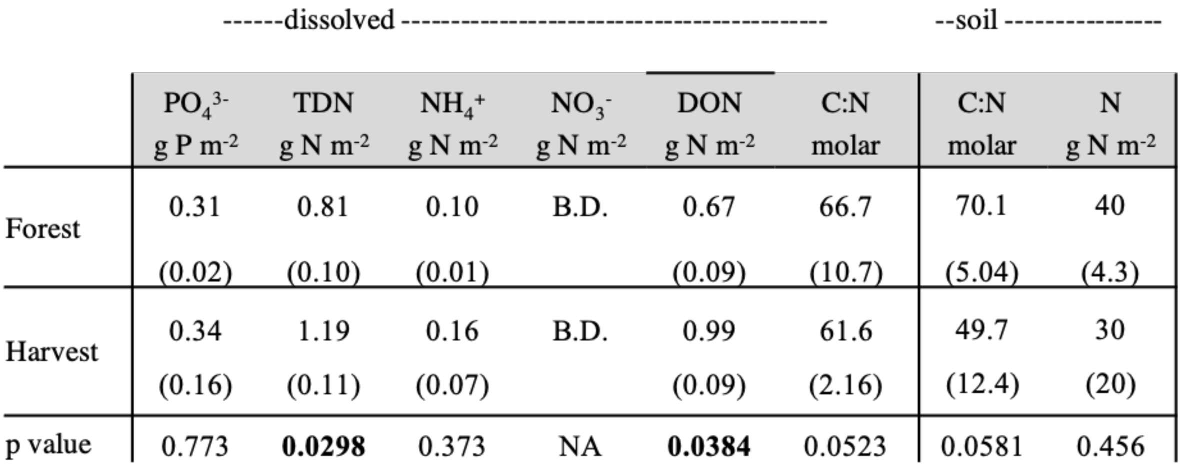
Table S6: Regression analysis among soil respiration, soil temperature, soil moisture and interactions in forest and harvested plots. R, T, and WC were measured concurrently at biweekly intervals during the snow-free season (May 1 - Nov 30) from 2013 to 2015. α= 0.05.

Plot type	**Variable**	**DF**	**Parameter Estimate**	**Standard Error**	**t**	**p-value**
Forest	Intercept	1	0.986	0.579	1.7	0.0892
	T_s	1	0.278	0.055	5.08	**<.0001**
	M_s	1	-0.037	0.019	-1.93	**0.0544**
	T_s x M_s	1	0.004	0.002	2.17	**0.0306**
Harvested	Intercept	1	1.543	0.432	3.57	0.0004
	T_s	1	0.145	0.032	4.60	**<.0001**
	M_s	1	-0.071	0.014	-4.99	**<.0001**
	T_s x M_s	1	0.006	0.001	5.58	**<.0001**

Table S7: Calibration equations for field measured soil water content (WC) at 5 cm depth in forest and harvested plots. Corrected WC derived from infiltration and evaporation experiments at residual and matrix saturation (see Table 2.4)

	Field WC (x)	Corrected WC (y)	Calibration Equation
Forest			
Residual	0.04	0.18	y = 1.5769x+ 0.1219
Matrix	0.17	0.39	
Harvested			
Residual	0.10	0.20	y = 2.0x
Matrix	0.23	0.46	

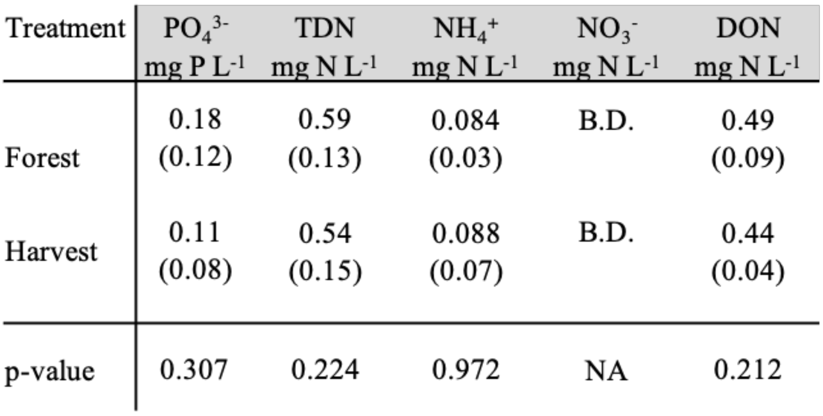
Table S8: Total annual lysimeter captured dissolved fluxes and soil properties. Total dissolved nitrogen (TDN), ammonium (NH_4^+), nitrate (NO_3^-), dissolved organic nitrogen (DON), orthophosphate (PO43-) and the C:N of DOM from O horizons. NO_3^- was below detection (B.D.). Mean carbon to nitrogen ratio (C:N) and total nitrogen (N) of organic horizon soil. One-way ANOVAs were used to assess significant differences between treatments (bolded, alpha = 0.05). Standard deviation of the mean of 3 plots per treatment provided in parentheses.



------dissolved -- --soil ---------------

	PO_4^{3-} $g\ P\ m^{-2}$	TDN $g\ N\ m^{-2}$	NH_4^+ $g\ N\ m^{-2}$	NO_3^- $g\ N\ m^{-2}$	DON $g\ N\ m^{-2}$	C:N molar	C:N molar	N $g\ N\ m^{-2}$
Forest	0.31 (0.02)	0.81 (0.10)	0.10 (0.01)	B.D.	0.67 (0.09)	66.7 (10.7)	70.1 (5.04)	40 (4.3)
Harvest	0.34 (0.16)	1.19 (0.11)	0.16 (0.07)	B.D.	0.99 (0.09)	61.6 (2.16)	49.7 (12.4)	30 (20)
p value	0.773	**0.0298**	0.373	NA	**0.0384**	0.0523	0.0581	0.456

Table S9: Concentrations of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), ammonium (NH_4^+), nitrate (NO_3^-), dissolved organic nitrogen (DON), and orthophosphate (PO_4^{3-}) of the total annual solution flux captured by lysimeters. NO_3^- was below detection (B.D.) One-way ANOVAs were used to test significant differences between treatments (α= 0.05).



Treatment	PO_4^{3-} $mg\ P\ L^{-1}$	TDN $mg\ N\ L^{-1}$	NH_4^+ $mg\ N\ L^{-1}$	NO_3^- $mg\ N\ L^{-1}$	DON $mg\ N\ L^{-1}$
Forest	0.18 (0.12)	0.59 (0.13)	0.084 (0.03)	B.D.	0.49 (0.09)
Harvest	0.11 (0.08)	0.54 (0.15)	0.088 (0.07)	B.D.	0.44 (0.04)
p-value	0.307	0.224	0.972	NA	0.212

Table S10: Optical properties and dissolved organic matter-metal associations. Specific UV absorbance measured at 254nm (SUVA). Slope ratio (SR) is the spectral slope at 275–295 nm divided by the spectral slope at 350–400nm, pH, and Fe and Al concentration in mature forest (F) and harvested (H) treatments. Bolded values show significant treatment differences on certain sampling dates. Values with the same letter within each analysis type column are not significantly different. Standard deviations of the mean of 12 lysimeters per treatment shown in brackets. ND = No data.

Date	DOC:DON (molar)		pH		SUVA L mg^{-1}		SR 275/350		[DOC] ppm		[TDP] ppm		[Fe] ppb		[Al] ppb		DOC:Fe (molar)		DOC:Al (molar)	
	F	H	F	H	F	H	F	H	F	H	F	H	F	H	F	H	F	H	F	H
17-Sep-13	**77.39**	**60.35**	**3.65**	**3.87**	**3.64**	**4.12**	0.74	0.73	71.09	60.94	0.37	0.32	178	258	569	707	2199	1606	461	259
	(9.97)	**(16.67**	**(0.15)**	**(0.15)**	**(0.22)**	**(0.18)**	(0.03)	(0.04)	(22.10)	(20.44)	(0.28)	(0.56)	(73)	(164)	(436)	(335)	(1178)	(1608)	(412)	(207)
07-Nov-13	69.38	66.80	4.07	4.12	**4.47**	**4.86**	0.76	0.76	30.35	28.85	0.26	0.07	**126**	**210**	366	563	1374	815	302	169
	(18.27)	(9.64)	(0.19)	(0.13)	**(0.19)**	**(0.32)**	(0.02)	(0.04)	(7.90)	(8.00)	(0.18)	(0.05)	**(53)**	**(126)**	(237)	(313)	(843)	(410)	(257)	(153)
15-Apr-14	51.93	57.05	ND	ND	4.65	4.89	0.81	0.83	28.38	15.18	0.19	0.04	83	108	255	305	**2091**	**806**	**435**	**141**
	(22.16)	(15.05)			(0.32)	(0.65)	(0.04)	(0.03)	(15.62)	(5.07)	(0.17)	(0.03)	(49)	(61)	(207)	(148)	**(1297)**	**(380)**	**(336)**	**(99)**
01-May-14	53.01	49.17	4.30	4.41	5.06	5.34	0.79	0.80	15.19	13.52	0.09	0.03	74	122	191	371	1417	667	**404**	**127**
	(10.16)	(11.67)	(0.17)	(0.13)	(0.25)	(0.51)	(0.02)	(0.01)	(4.68)	(4.88)	(0.07)	(0.03)	(55)	(70)	(162)	(172)	(1013)	(340)	**(439)**	**(142)**
20-May-14	48.86	49.47	4.99	5.13	**5.12**	**5.47**	0.082	0.83	11.21	13.48	0.05	0.04	54	107	**146**	**359**	1302	632	**354**	**107**
	(6.08)	(12.14)	(0.31)	(0.15)	**(0.20)**	**(0.28)**	(0.02)	(0.01)	(2.03)	(5.02)	(0.02)	(0.06)	(40)	(54)	**(130)**	**(146)**	(676)	(280)	**(297)**	**(72)**
10-Jun-14	43.29	35.89	4.84	4.84	4.95	4.87	0.78	**0.76**	45.08	31.91	0.23	0.29	137	171	393	470	1800	1072	400	187
	(5.36)	(11.19)	(0.54)	(0.20)	(0.54)	(0.62)	(0.05)	(0.04)	(15.50)	(10.57)	(0.17)	(0.37)	(58)	(105)	(269)	(191)	(1021)	(486)	(319)	(110)
08-July-14	**64.07**	**41.63**	ND	ND	**4.06**	**4.64**	0.74	0.76	62.27	37.17	0.23	0.16	156	185	439	484	**2118**	**1091**	461	192
	(12.40)	**(16.95)**			**(0.19)**	**(0.46)**	(0.023)	(0.034)	(19.08)	(11.77)	(0.12)	(0.12)	(55)	(99)	(286)	(163)	**(1049)**	**(409)**	(305)	(86)
Snow 02-Apr-14	ND	ND	ND	ND	2.17	1.51	0.69	2.60	7.2	3.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

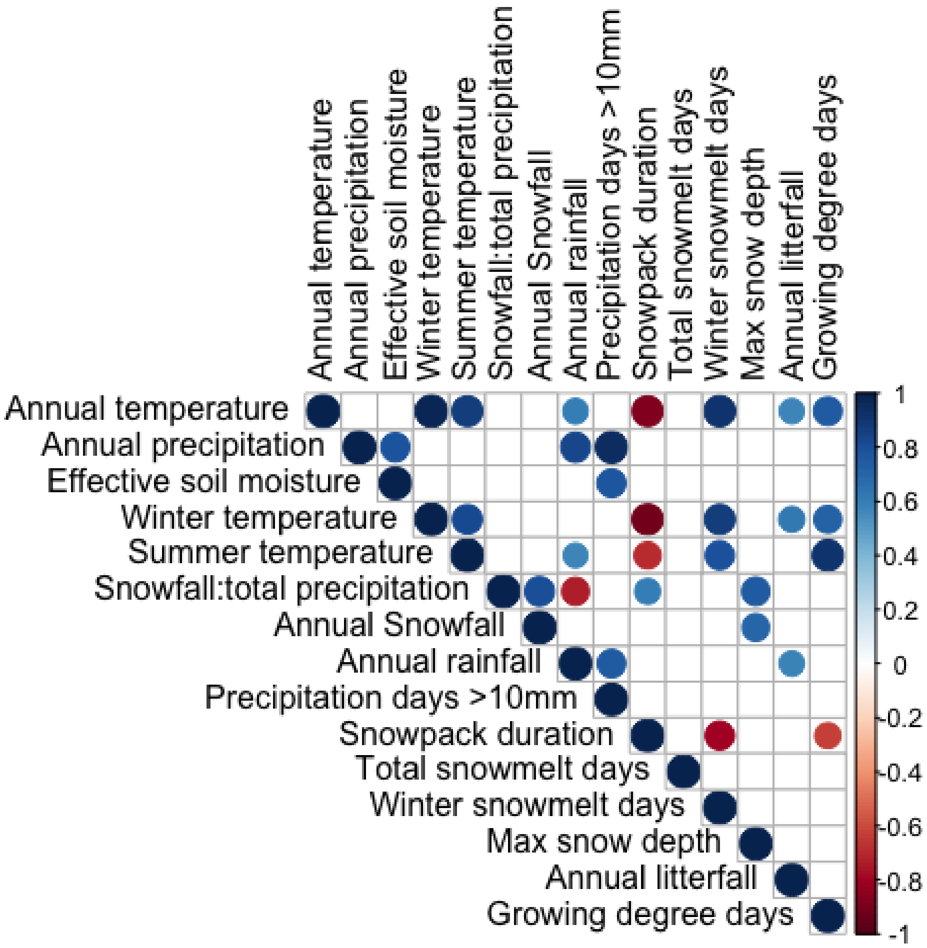


Figure S1: Correlation matrix of hydrometeorological variables included in multiple hypothesis testing.