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

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Abstract. Dissolved organic matter (DOM) mobilized from the organic (O) horizons of forest soils is a

10   temporally dynamic flux of carbon (C) and nutrients, and the fate of this DOM in downstream pools is dependent on the rate and pathways of water flow as well as its chemical composition. Here, we present observations of the composition of DOM mobilized weekly to monthly from O horizons in mature forest and adjacent harvested treatment plots. The study site was experimentally harvested, without replanting, 10-years prior to this study. Thus, the treatments differ significantly in terms of forest stand and soil properties, and

15   interact differently with the regional hydrometeorological conditions. This presented an opportunity to investigate the role of forest structure relative to environmental variation 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 harvested (H) treatment compared to the forest (F) treatment, however, neither phosphate or ammonium fluxes differed by treatment type. On a short-term basis in both H and

20   F treatments, 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 negatively correlated to the C:N of DOM. These results suggest common seasonal controls on DOM mobilization regardless of harvesting treatment. Optical characterization of seasonally representative samples additionally supported a stronger control of season over harvesting. The chemical character of DOM mobilized during winter and

25   snowmelt: lower C:N, higher SUVA and lower molecular weight of CDOM (higher spectral slope ratio), 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 regardless of harvesting impact. Despite the higher proportion of aromatic DOM in

30   the snowmelt samples, its lower molecular weight and rapid delivery from O to mineral horizons suggests that the snowmelt period is not likely to be a significant period of DOM sequestration by mineral soil. Rather, the higher molecular weight, high C:N DOM mobilized during slow and relatively infrequent delivery during summer and rapid, frequent delivery during autumn are more likely to support periods of mineral soil sequestration and increased export of fresher terrestrial DOM, respectively. These observed seasonal dynamics

35   in O horizon DOM suggest the predicted decreases winter and spring snowfall and increasing autumn and winter rainfall with climate warming in this region will enhance mobilization of DOM that is more reactive to mineral interactions in deeper soil, but also more biological and photoreactive in the aquatic environment. Understanding the downstream consequences of this mobilized DOM in response to these shifts in precipitation timing and form can improve our ability to predict and manage forest carbon balance but requires understanding

40   the response of landscape hydrology to these changing precipitation regimes.

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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. Jones and Kielland, 2012; Hensgens et al., 2020), as well as transformation and fate in mineral soil (Kothawala et al., 2008), 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 the knowledge gained from extraction studies into the larger catchment scale context. For instance, these measurements can more directly inform regional chromatography (i.e. Kaiser and Kalbitz, 2012; Shen et al., 2014) and terrestrial-to-aquatic carbon flux conceptual models (i.e. Tank et al., 2018), which further allow us to assess the impacts of disturbances such as harvesting and climate change on landscape carbon balance (Casas-Ruiz et al. 2023).

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 and Likens, 1988; 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), 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 soil C:N and DOM C:N. 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 and forest floor mosses (Philben et al. 2018; Hensgens et al., 2020). Nitrogen-limitations can also affect decomposition and soil C accumulation (Averill and Waring, 2018), 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 effects on soil DOM. These dynamics are further impacted by snow-cover,

80   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 an efficient
technique for describing broad DOM compositional differences in surface waters and identifying terrestrial
DOM sources (Helms et al., 2008; McKnight et al., 2001; Jaffé et al., 2008; Berggren and Giorgio, 2015). These

85   techniques 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

90   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

95   (Guggenberger and Zech, 1993; Kaiser and Kalbitz, 2012). However, *in situ*, the consequences of these
transformations are dependent on the rate and pathways of water and DOM composition and flow. Clarification
is needed on the controls over both the rate and composition of mobilized DOM which could then inform
potential mineral stabilization versus export potential of soil DOM from upland forests under varying
hydrometeorological conditions.

100   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 the situation when clear-

105   cut, or otherwise disturbed, boreal black spruce forests remain open for long periods of time. As seasonal and
decadal scale 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 as part of a case study. Previously, we demonstrated that the thickness of the organic horizon was reduced

110   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. Focusing on the hot spots and moments of boreal forest DOM

115   mobilization likely sensitive to climate change, these results help identify the "top-down" controls on carbon and nutrient storage in boreal forest mineral soils and potential fate of forest soil DOM exported to aquatic systems.

2 Materials and Methods

120   ### 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, located in the Maritime Low Boreal Ecoclimate (Lbm) of the Ecoregions Working Group (1989), and is dominated by black spruce (*Picea mariana*).

125   The site is underlain by humo-ferric podzolic soils (Soils Classification Working Group, 1998) that have developed on fresh glacial, poorly sorted till deposits of granite, porphyry, sandstone, and siltstone clasts (Batterson and Catto 2001) with quartz most abundant, followed by plagioclase, muscovite, chlorite, K-feldspar and biotite (Patrick et al., 2022). The surrounding boreal landscape is characterized by a mosaic of different age classes resulting from a history of periodic disturbance, including that from forest harvesting. The climate of the

130   study region is characterized by winters with consistent snowpack for 4-5 months of the year from December to April. The area receives on average 1095 mm of precipitation annually, with approximately 40% as snow, with a mean annual temperature of 3.6°C (Environment Canada Climate Normals, Deer Lake Airport 1981–2010). During the study year total precipitation was 1402 mm with 516 mm (37%) of that as snowfall water equivalent, and snowpack at the start of snowmelt period during the study ranged from 83 to 110 mm snowfall water

135   equivalent across the study plots, and was higher in the harvested plots (Bowering et al., 2020) similar to the long-term average in the region (Environment Canada Climate Normals, Deer Lake Airport 1981–2010). The site consists of 2 hectares divided into eight 50 x 50 m plots (Fig. S1). 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

140 deciduous trees left standing. The close proximity of the plots enabled comparison of mature and harvested forest areas over a similar slope, aspect, elevation and soil type and thus represents a case study of the harvesting effects within the context of seasonal variation. The two treatments of this case study will be referred to as harvested (H) and mature forest (F) throughout. In this study we used three plots of each treatment as indicated in Fig. S1.

145 Following common forestry practices for the area, the harvested plots were not replanted following clear-cutting. Moss coverage persisted in the H plots where a larger proportion was *Sphagnum sp*. as compared with F plots where moss cover was dominated by *Hylocomium splendens*. The harvested plots also consisted of naturally regenerated herbs (including *Cornus canadensis*, *Chamerion angustifolium*, *Vaccinium angustifolium*) and shrubs (*Alnus alnobetula* (Ehrh.)) and few young conifers (ages 5-8 years; below 1.5 m in height) at much

150 lower density than the adjacent mature stands (see Fig. S1 for aerial image taken year after lysimeter installation). Average (±SD) organic horizon thickness was 8.2 ± 0.6 and 4.3 ± 0.6 cm, and carbon stocks were 2.4 ± 0.2 and 1.3 ± 0.3 kg C m^{-2} in the forest and harvested plots, respectively (Bowering et al., 2020). Further information on site preparation and conditions can be found in Moroni et al., (2009) while further soil features (e.g. hydrologic properties) can be found in Bowering et al. (2020).

155 **2.2 Sampling Design, 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., 2000). A detailed description of the

160 lysimeter design can be found in Bowering et al. (2020) and illustration of the design and installation of the lysimeters is provided in figure S2. Installation of lysimeters began in July 2012 and was completed the following spring in May 2013. The design includes the fixed effect of stand type (mature and harvested forest) at a scale above the individual lysimeters. Four lysimeters were installed in each of the three plots of each treatment for a total of 12 mature forest (F) lysimeters and 12 harvested (H) lysimeters (Fig. S1). Collection

165 began in July 2013 and sampling of all lysimeters in 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

170 within 24 hours of collection, and stored at 4°C in the dark until analysis. This approach, capturing both vertical and lateral flow, previously revealed an effect of stand type on the mobilization of dissolved organic carbon with the harvested plots exhibiting a nearly 50% increase in DOC mobilization relative to the mature forest plots (Bowering et al. 2022).

2.3 Environmental Monitoring

175 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

180 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

185 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 H) or throughfall (in F) 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

190 al., 2020).

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}

195 ^{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}). Measures of Fe and Al and their ratio to DOC were included to track reactive metals relevant in these organic soils because of their role in formation of organo-mineral complexes (TORN et al., 1997) as well as their translocation into O horizons from the lower mineral horizon via fungal activity (Clarholm and Skyllberg, 2013).

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 without any 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.

2.6 Absorbance Properties

For optical property measures, a subset of lysimeter samples from forest and harvested treatments was selected to broadly represent the four seasons (Table 5). 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 (S_R) 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 S_R), 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 4A) relative to season (Figure 4B).

2.7 Statistical Analysis

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 1 and S1) using the 'nlme' package (Pinheiro et al., 2022). Post-hoc Tukey tests using the 'lsmeans' package (Lenth, 2016) were used to determine significant differences between H and F treatments on individual collection days (Figures 1 and 2; asterisks). Further RM-LMMs were used to assess the effects of season and treatment on DOM fluxes (Table 3) and to assess the effects of collection day and treatment on absorbance properties, metals and their ratio to DOC (Table 4). Diagnostic autocorrelation plots were generated using the ACF function in R (Mangiafico 2016) to assess autocorrelation associated with lysimeter measurements. These plots demonstrate that each lag point is smaller than the proceeding lag point signifying a lack of autocorrelation. 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 S1 and S2). Annual fluxes by treatment are shown in Figure 1 and Figure 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). 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 (Figure 4) was performed using the ggfortify (Tang et

al., 2016) and factoextra (Kassambara and Mundt, 2017). All statistical analyses were performed using RStudio version 1.0.136.

3 Results

3.1 Annual fluxes and concentrations in harvested and forest treatments

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 1d,e and Table 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 average C:N of DOM were not different between H and F treatments. However, the C:N of DOM in the H treatment was higher than the C:N of the O horizon soil from which it was derived, while the C:N of DOM in the F treatment was similar to the C:N of the O horizon soil (Figure 2b,c). Despite treatment differences in annual fluxes of TDN and DON (Figure 1 and Table S1), the average annual concentrations of all solutes did not differ between treatments (Table S2).

3.2 Intra-annual fluxes and concentrations in harvested and forest treatments

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 1 and 2), indicated by the significant effect of collection day ($p<0.001$; Table 1; Table S3). There was also an interactive effect of treatment and day on all concentrations and fluxes (Table 1 and Figures 1,2) though 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. An effect of treatment was detected for DON fluxes only ($p = 0.0208$) with H often exceeding F treatment fluxes. All concentrations were positively correlated to soil temperature (Table 2a), except for DON in the F treatment, and all concentrations were

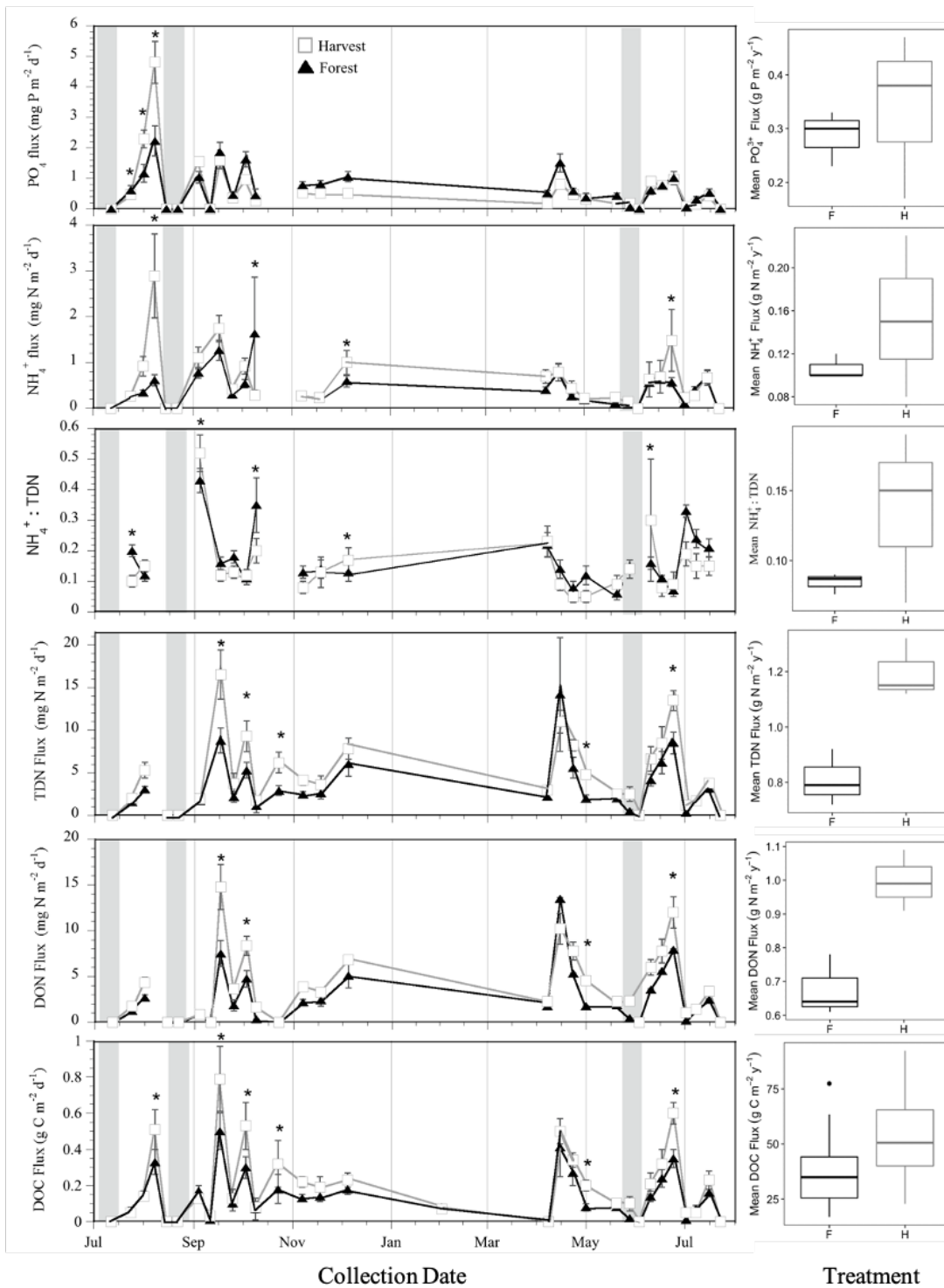



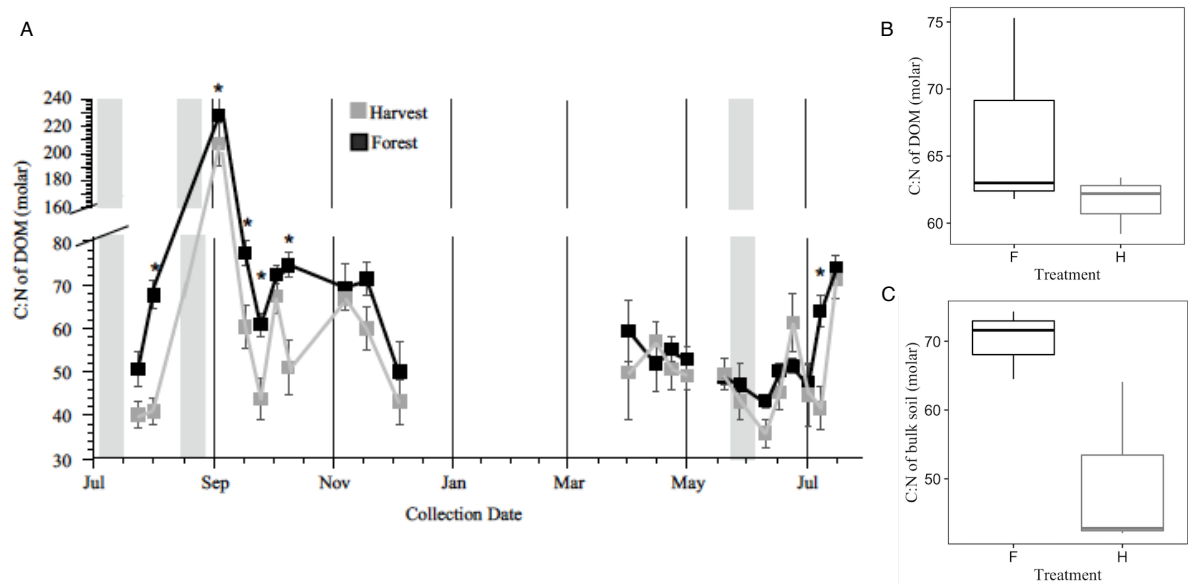
Figure 1. Intra-annual variation of lysimeter captured (a) phosphate (PO_4^{3-}) fluxes (b) ammonium (NH_4^+) fluxes and (c) total dissolved nitrogen (TDN) fluxes, (d) ammonium to total dissolved nitrogen ratio (NH_4^+/TDN), and (e) Dissolved organic nitrogen (DON) from soil organic horizons in mature 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).

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Figure 2. Intra-annual variation of the dissolved organic carbon (DOC) to dissolved organic nitrogen (DON) ratio collected by lysimeters (a). 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

315   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. Boxplot of C:N of DOM in harvest(H) and forests(F) (b) compared to organic horizon C:N in H and F (c). Boxplots show the median and confidence intervals of plot scale annual means (n=3 per plot type).

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Table 1. Repeated measures linear mixed effects model results assessing the effect of collection day and the interaction with treatment on concentrations of total dissolved nitrogen (TDN), ammonium (NH_4^+), dissolved organic nitrogen (DON), orthophosphate (PO_4^{3-}), as well as the ratios between NH_4^+ and TDN and between dissolved organic carbon and DON (DOC:DON).

[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**

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Table 2. 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.

		df	A. soil temperature		B. soil moisture		C. water input	
			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

A Bonferroni correction was applied to account for Type 1 Error (alpha = 0.05/3 = 0.017).

negatively correlated with water input (Table 2c), 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 2c), except NH_4^+ and PO_4^{3-} in H. No relationship was observed between concentrations and fluxes with soil moisture, except the negative correlation with DOC concentration in the H treatment (Table 2b). Soil moisture was negatively correlated with the C:N of DOM in both treatments.

3.3 Seasonal fluxes and concentrations in harvested and forest treatments

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). Soil water fluxes were always greater through the O horizons of H treatment compared to F and the four seasonal periods (summer, autumn, winter and snowmelt/spring; see *Seasonal Designations* in methods) exhibited four different cumulative water fluxes (Figure 3a). The largest cumulative water fluxes in H and F treatments 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; $p<0.0001$), 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 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 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 3d). The variation in values for the water, DOC and DON flux is likely a result of variation in litterfall and throughfall across the plots overall and observed through the individual lysimeters (Bowering et al., 2020).

There was an effect of collection date on all absorbance properties (Table 4a-d; $p<0.0001$), and an effect of treatment on SUVA only where values were often higher in the H treatment ($p = 0.0033$). An interactive effect was observed for $SS_{275-295nm}$ ($p = 0.001$) and $SS_{350-395nm}$ ($p = 0.0045$). An effect of collection date on both Fe and Al (Table 4e,f; $p<0.0001$) was also observed but only Fe exhibited a treatment effect ($p = 0.0332$) with higher

concentrations in the H treatment. There was an effect of collection day on DOC:Fe (Table 4g; p<0.0001) and no effect of harvesting while only a harvesting effect was observed with DOC:Al with higher values observed in the F relative to H treatment (Table 4h; p=0.0247). The elevated values and variability in DOC:Fe and DOC:Al as well as the lack of collection date effect for DOC:Al indicates little evidence for relevant seasonal controls on proportions of these reactive metal that might impact the fate of organic horizon DOC. 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 (Table 5). The snow $SUVA_{254nm}$ values were lower than all lysimeter samples and the LMW spectral slope ($SS_{275-295nm}$) was higher than lysimeter samples collected during snowmelt. The HMW spectral slope ($SS_{350-395nm}$) of snow was higher in F than H treatments, 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 S_R value for the H (2.60) in comparison to the F (0.69) treatment snow. This is likely attributable to greater litterfall sources of DOM in the F treatment plots given the greater needle litterfall on the snow surface and higher input of DOC from snow in the forest plots (2.1 versus 1.3 g DOC m^{-2} y^{-1}for F and H plots, respectively; Bowering et al., 2020).

A principal component analysis (PCA) including absorbance properties ($SUVA_{254nm}$, $SS_{275-295nm}$, $SS_{350-395nm}$, and S_R), the C:N of DOM and DOC:Fe grouped by treatment (Figure 4a) and season (Figure 4b) demonstrated the overriding effect of season compared to harvesting. PC1 and PC2 describe 41% and 26.6% of the dataset variability, respectively. Seasonally, autumn soil DOM is characterized by higher molecular weight CDOM, signified by higher $SS_{350-395nm}$ and lower S_R, as well as higher C:N of DOM, while winter and snowmelt samples are characterized by lower molecular weight CDOM signified by higher S_R, and to a lesser extent higher $SUVA_{254nm}$ and lower C:N. Harvested and forested samples were weakly separated by SUVA and DOC:Fe, with higher values of both in the H treatment.

425 **Table 3.** Repeated measures linear mixed effects model 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.

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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
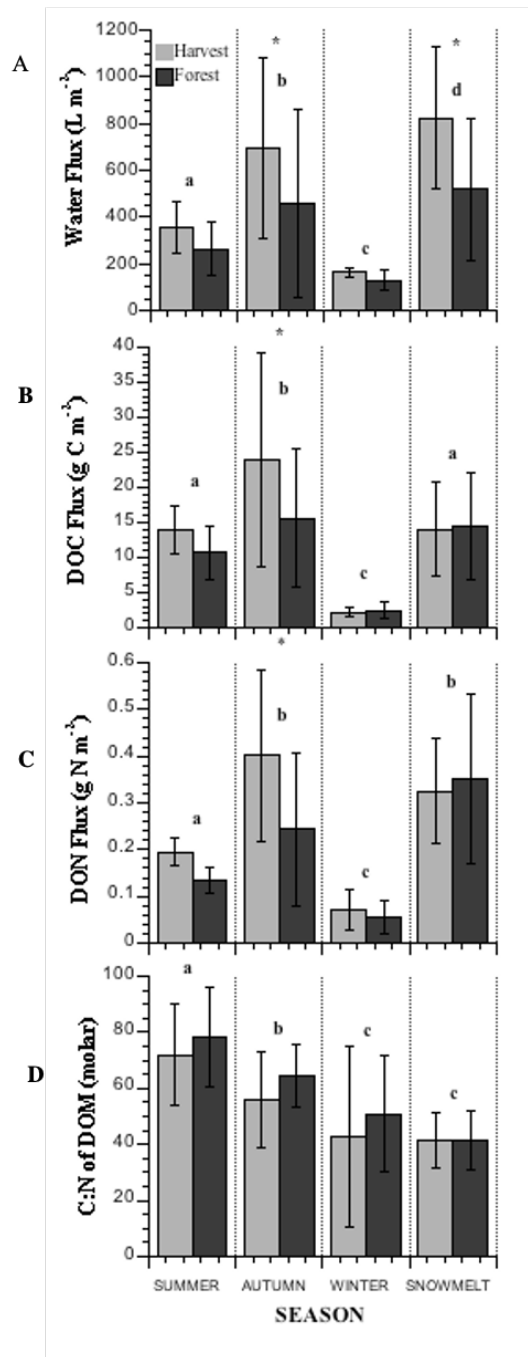
Figure 3. Total seasonal fluxes of water, dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and the C:N of DOM in the mature forest (F) and harvested (H) treatments. Seasonal designations are described in the methods section. Seasonal periods sharing the same letter are not significantly different. Asterisks indicate significant differences between treatments. Error bars show the standard deviation of 12 lysimeters per treatment per season.

475

Table 4. Repeated measures linear mixed effects model 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).

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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	**0.0257**
Date	6	1.96941	0.0754
Treatment:Date	6	0.56551	0.757

(a)   **(b)**
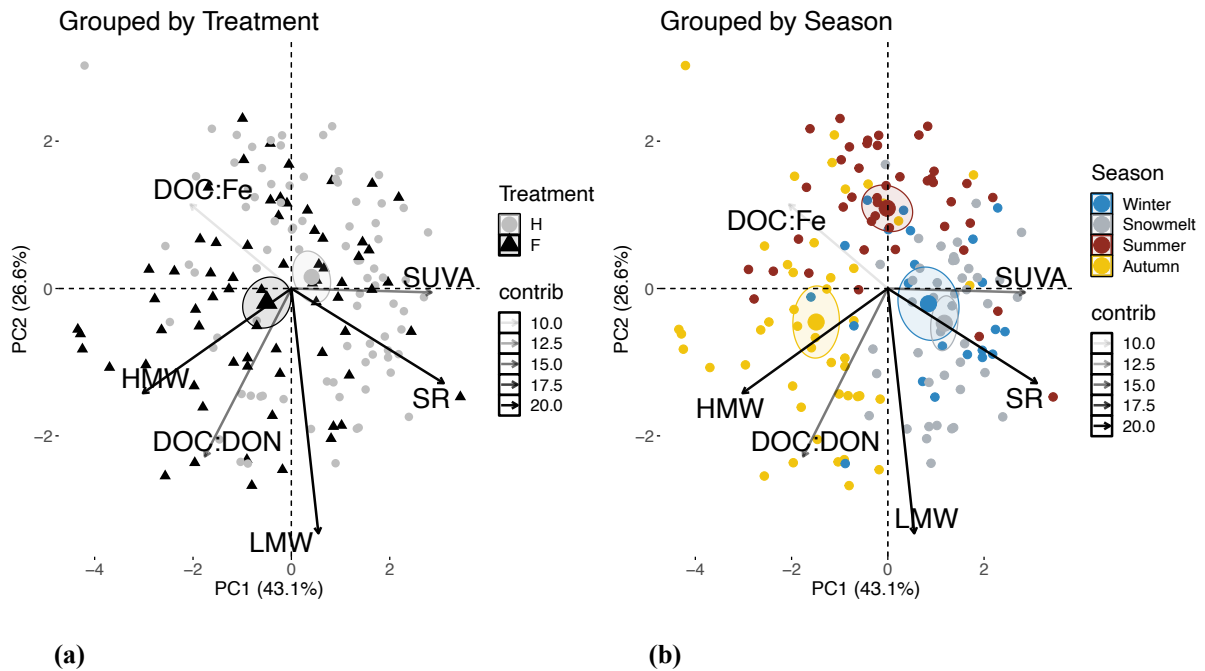
Figure 4. Principal component analysis biplots used to explore the predominant variables describing the harvesting effect compared to the seasonal effect on the composition of mobilized dissolved organic matter (DOM). Variables included are dissolved organic carbon (DOC) to iron ratio (DOC:Fe), the spectral slope for 350 to 395 nm (SS350-395nm) indicative of high molecular weight (HMW) DOM, the spectral slope for 275 to 295 nm (SS275-295nm) 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 Winter, Snowmelt, Summer and Autumn. Vectors are shaded according to their combined percent contribution (contrib) to PCA1 and PCA2. Ellipses represent the 95% confidence interval around each group mean.

Table 5. 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

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 decadal time scale effect of forest harvesting. Clear-cut harvesting immediately reduces the interception of water 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), clear-cutting increased the mobilization of dissolved organic nitrogen (DON) on weekly to annual time scales. The relative temporal patterns of DOM composition, however, were similar in mature forest and harvested treatments supporting other work which describe a dominating control of environmental factors compared to soil

composition on DOM composition (Cronan and Aiken, 1985; Kaiser et al., 2001; Fröberg et al., 2011). The
560   compositional patterns observed in this study are indicative of DOM from fresh plant and microbial origin in the
summer through autumn, and a shift to DOM from microbial biomass and microbially processed materials
underneath a consistent snowpack in winter and during snowmelt. These seasonal shifts highlight a potential
sensitivity of DOM composition to the changing climate, particularly in northern forests experiencing snowpack
reductions and an increased autumn-winter wet period. The more dynamic snowpacks (those experiencing melt)
565   associated with warmer winters can increase winter soil water fluxes, and may consequently drive the
mobilization of less processed soil DOM (i.e. higher HMW and C:N) during winter. This hypothesized soil
response to increasingly warmer winters in this region is consistent with observed increases in river DOM
export attributed to enhanced wintertime exports from a large catchment in a similar landscape further south
(Huntington et al. 2016). The temporal and compositional changes observed here have implications for the
570   ultimate lability, physiochemical and biological, and fate of soil DOM within northern forests and once exported
to aquatic systems.

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

575   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 lower 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 uptake or immobilization of
580   N (Kirschbaum, 1995; Conant et al., 2011; Hilli et al., 2008). While greater proportions of soil 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;
Bowering et al., 2020). Additional concurrent processes known to affect DOM production at high seasonal
585   temperatures are soil drying and rewetting cycles (Fierer and Schimel, 2002), and rhizodeposition (Weintraub et
al., 2006; Heijden et al., 2008). These processes could contribute to mobilized DOC in summer, although the
later would contribute LMW DOM instead of the HMW DOM observed (Giesler et al., 2007).

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 1), highlighting the likelihood 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 (Ste-Marie and Paré, 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; Schimel and Bennett, 2008; Näsholm et al., 1998) with plants and microbes competing for low molecular weight DON, such as amino acids and peptides (Farrell et al., 2014). Combined, these processes limit the amount of ON available for mobilization during summer and contribute to the elevated C:N of the DOM observed during the summer period.

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. 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 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 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, 2008), 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.

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

620   Fluxes of low C:N, low molecular weight DOM occurring during winter and the following snowmelt period were 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

625   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

630   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 is indicative of a greater microbial contribution to the DOM during this period. Interestingly, the high SUVA$_{254nm}$ was coupled with high S_R observed in winter and snowmelt samples, suggests the mobilization of relatively more aromatic, but of relatively lower molecular weight in comparison to soil DOM from summer and

635   autumn. SUVA and S_R are typically shown to be negatively correlated in surface water indicative of high molecular weight aromatic DOM (Helms et al. 2008). These results support the occurrence of microbial degradation of soil organic matter in the absence of fresh litter inputs underneath the snowpack, increasing the solubility of aromatic compounds such as lignin in soil (Malcolm, 1990; Hansson et al., 2010; Klotzbücher et al., 2013) enhancing aromaticity and reducing the relative molecular weight of the CDOM. Congruent with this,

640   the lower DOC:DON is attributable to microbial metabolites or proteinaceous products released following this long period of degradation in absence of fresh plant inputs as observed in soil incubations (Kalbitz, 2003). These observations are also consistent with the initial steps in the synthesis of CDOM or humic substances; the fungal breakdown of lignin-cellulose as part of the polyphenol theory of humic substance formation processes (Stevenson 1994) also observed in organic rich peat (Prijac et al., 2022).

4.4 The seasonal variability of soil DOM composition has implications for its fate in a changing climate

This study demonstrates that the composition of mobilized soil DOM is similarly variable between sites of contrasting forest stand and soil properties. Clear-cut harvesting causes changes to forest water balance, through immediate removal of the canopy and longer-term reduction of the O horizon thickness, and results in larger quantities of mobilized DOM on decadal time scales. Despite this, the response of soil DOM composition to season suggests that the mobilization of soluble materials in the two treatments are controlled by similar responses to environmental conditions. Optical properties and the C:N of DOM during summer and autumn, compared to winter and snowmelt were reflective of shifts from fresh plant-derived to microbial-derived DOM. This compositional shift 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 are often near 0°C, and the projected 7°C increase in mean winter temperature (Finnis and Daraio, 2018) is likely to cause increases in winter rain and melt events, soil water fluxes and, consequently, mobilization of less processed soil DOM. The delivery of less processed DOM, exhibiting a higher MW CDOM fraction, could result in increased mineral soil adsorption (Guggenberger and Zech, 2002; Kaiser and Guggenberger, 2000; Lilienfein et al., 2004; Kothawala et al., 2008) dependent on the texture and mineralogy of the underlying soil and including the pathway and resident time of water (e.g. Oades, 1988; Marschner and Kalbitz, 2003; Patrick et al., 2022; Slessarev et al., 2022).

Research conducted in these same and similar forest sites underlain by podzolic soils indicate adsorption of DOM within shallow mineral soils is highly dynamic and dependent upon seasonal conditions (e.g. solution pH), and reactive Al availability and its saturation with carbon. The siliciclastic sedimentary till in the study area provides an ample source of reactive Fe and Al to support the generation of organo-mineral complexes via co-precipitation of DOM and these metals as well as adsorption onto existing complexes (Patrick et al. 2022). In some hillslope locations of this study site, deeper mineral horizons have a large potential for DOM adsorption dependent on infiltration depths that may occur with the enhanced fall and winter rainfall expected in this region (Patrick et al., unpubl. data). Therefore, the differences in DOM composition between fall and spring snowmelt further support potential for enhanced formation of these complexes with the expected decreases in spring snow melt and increasing autumn and winter rainfall and infiltration.

675 Warmer winters are linked to enhanced catchment export of DOM in an area just south of our study region (Huntington et al. 2016), consistent with regional evidence for enhanced soil DOM mobilization with warming winters (Bowering et al. 2022), and suggests a shift to increased export of fresher terrestrial DOM. In the freshwater environment fresher terrestrial DOM, characterized by an increased high MW fraction, degrades more readily relative to low MW, N-rich DOM (Kellerman et al., 2015; Köhler et al., 2013; Kothawala et al.,

680 2014). However, fresher terrestrial DOM also contributes more to sediment burial in high latitude lakes through light and microbial mediated flocculation (Wachenfeldt et al., 2008, 2009), and can have a greater potential to remain buried longer relative to more microbially derived OM (Gudasz et al., 2012). Enhanced export of more labile, higher MW DOM coupled with enhanced water input, and thus lower water residence times in the aquatic environment such as in this study region, suggests increases in a high MW DOM fraction throughout the

685 aquatic environment (Weyhenmeyer et al., 2014) and potential for lake burial or export to the marine environment opposite of those regions experiencing decreases in precipitation (Catalán et al., 2016). Therefore, the ultimate impact of these shifts in forest soil DOM composition on the carbon balance of these landscapes depends on both the connectivity with and properties of deep mineral soils as well as the net effect on downstream aquatic processes of burial and metabolism.

690

5 Conclusion

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, however these effects are dependent on the type of snowpack change (Stark et al., 2020). In

695 this wet eastern boreal region, snowpacks are deep (>80 cm maximum snow depth) and are likely to change with warmer winters, increases in rain on snow events, and ice incasement, with soil freezing being a less significant concern in comparison to forests with shallower snowpacks. Future work capturing variable snowpack years (either within or across sites) and impacts on landscape and small catchment hydrology is needed. This would help clarify the relative importance of these changes on the chemical character of soil

700 organic matter and mobilized soil DOM, and inform their implications for the fate of DOM within deeper mineral soils and the aquatic environment. Such efforts would improve our understanding of the response of soil organic matter to a rapidly changing climate and our ability to manage forest carbon balance in boreal landscapes.

Data availability

All data associated with this study can be found at this publically available site:
https://github.com/ArkosicGreywacke/PBEWA/tree/main/Hillslope/Pynn's%20Brook%20Experimental%20Forest%20Lysimeters%202013-2014

Author Contribution

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 significant input from SEZ and editing from KAE and SEZ.

Competing interests. The authors declare that they have no conflict of interest.

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References

Averill, C. and Waring, B.: Nitrogen limitation of decomposition and decay: How can it occur?, Global Change Biol, 24, 1417–1427, https://doi.org/10.1111/gcb.13980, 2018.

Batterson, M.J., Catto, N.R.: Topographically-controlled deglacial history of the Humber River basin, western Newfoundland, Geographie Physique et Quaternaire, 55, 213–228, https://doi.org/10.7202/006851ar., 2001.

Berggren, M. and Giorgio, P. A.: Distinct patterns of microbial metabolism associated to riverine dissolved organic carbon of different source and quality, J Geophys Res Biogeosciences, 120, 989–999, https://doi.org/10.1002/2015jg002963, 2015.

Bowering, K. L., Edwards, K. A., Prestegaard, K., Zhu, X., and Ziegler, S. E.: Dissolved organic carbon mobilized from organic horizons of mature and harvested black spruce plots in a mesic boreal region, Biogeosciences, 17, 581–595, https://doi.org/10.5194/bg-17-581-2020, 2020.

740 Brooks, P. D., Grogan, P., Templer, P. H., Groffman, P., Öquist, M. G., and Schimel, J.: Carbon and Nitrogen Cycling in Snow-Covered Environments: Carbon and nitrogen cycling in snow-covered environments, Geogr Compass, 5, 682–699, https://doi.org/10.1111/j.1749-8198.2011.00420.x, 2011.

Campbell, J. L., Reinmann, A. B., and Templer, P. H.: Soil Freezing Effects on Sources of Nitrogen and Carbon Leached During Snowmelt, Soil Sci Soc Am J, 78, 297–308, https://doi.org/10.2136/sssaj2013.06.0218, 2014.

745 Casas-Ruiz, J. P., Bodmer, P., Bona, K. A., Butman, D., Couturier, M., Emilson, E. J. S., Finlay, K., Genet, H., Hayes, D., Karlsson, J., Paré, D., Peng, C., Striegl, R., Webb, J., Wei, X., Ziegler, S. E., and Giorgio, P. A. del: Integrating terrestrial and aquatic ecosystems to constrain estimates of land-atmosphere carbon exchange, Nat Commun, vol. 14, 14, 1571, https://doi.org/10.1038/s41467-023-37232-2, 2023.

Catalán, N., Marcé, R., Kothawala, D. N., and Tranvik, Lars. J.: Organic carbon decomposition rates controlled 750 by water retention time across inland waters, Nat Geosci, 9, 501–504, https://doi.org/10.1038/ngeo2720, 2016.

Clarholm, M. and Skyllberg, U.: Translocation of metals by trees and fungi regulates pH, soil organic matter turnover and nitrogen availability in acidic forest soils, Soil Biology Biochem, 63, 142–153, https://doi.org/10.1016/j.soilbio.2013.03.019, 2013.

Conant, R. T., Ryan, M. G., Ågren, G. I., Birge, H. E., Davidson, E. A., Eliasson, P. E., Evans, S. E., Frey, S. 755 D., Giardina, C. P., Hopkins, F. M., Hyvönen, R., Kirschbaum, M. U. F., Lavallee, J. M., Leifeld, J., Parton, W. J., Steinweg, J. M., Wallenstein, M. D., Wetterstedt, J. Å. M., and Bradford, M. A.: Temperature and soil organic matter decomposition rates - synthesis of current knowledge and a way forward, Global Change Biology, 17, 3392–3404, https://doi.org/10.1111/j.1365-2486.2011.02496.x, 2011.

Cortina, J., Romanyà, J., and Vallejo, V. R.: Nitrogen and phosphorus leaching from the forest floor of a mature 760 Pinus radiata stand, Geoderma, 66, 321–330, https://doi.org/10.1016/0016-7061(95)00006-a, 1995.

Cronan, C. S. and Aiken, G. R.: Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York, Geochim Cosmochim Ac, 49, 1697–1705, https://doi.org/10.1016/0016-7037(85)90140-1, 1985.

Ecoregions Working Group.: Ecoclimate regions of Canada. Ecol. Land Class. Series No. 23. Environment 765 Canada, Canadian Wildlife Service, Ottawa, ON. 118 pp, https://d1ied5g1xfgpx8.cloudfront.net/pdfs/23092.pdf, 1989.

Farrell, M., Prendergast-Miller, M., Jones, D. L., Hill, P. W., and Condron, L. M.: Soil microbial organic nitrogen uptake is regulated by carbon availability, Soil Biology Biochem, 77, 261–267, https://doi.org/10.1016/j.soilbio.2014.07.003, 2014.

770 Fierer, N. and Schimel, J. P.: Effects of drying–rewetting frequency on soil carbon and nitrogen transformations, Soil Biology Biochem, 34, 777–787, https://doi.org/10.1016/s0038-0717(02)00007-x, 2002.

Fröberg, M., Hansson, K., Kleja, D. B., and Alavi, G.: Dissolved organic carbon and nitrogen leaching from Scots pine, Norway spruce and silver birch stands in southern Sweden, Forest Ecology and Management, 262, 1742–1747, https://doi.org/10.1016/j.foreco.2011.07.033, 2011.

775 Giesler, R., Högberg, M. N., Strobel, B. W., Richter, A., Nordgren, A., and Högberg, P.: Production of dissolved organic carbon and low-molecular weight organic acids in soil solution driven by recent tree photosynthate, Biogeochemistry, vol. 84, 84, 1–12, https://doi.org/10.1007/s10533-007-9069-3, 2007.

Gödde, M., David, M. B., Christ, M. J., Kaupenjohann, M., and Vance, G. F.: Carbon mobilization from the forest floor under red spruce in the northeastern U.S.A., Soil Biology Biochem, 28, 1181–1189,
780 https://doi.org/10.1016/0038-0717(96)00130-7, 1996.

Groffman, P. M., Driscoll, C. T., Durán, J., Campbell, J. L., Christenson, L. M., Fahey, T. J., Fisk, M. C., Fuss, C., Likens, G. E., Lovett, G., Rustad, L., and Templer, P. H.: Nitrogen oligotrophication in northern hardwood forests, Biogeochemistry, 141, 523–539, https://doi.org/10.1007/s10533-018-0445-y, 2018.

Gudasz, C., Bastviken, D., Premke, K., Steger, K., and Tranvik, L. J.: Constrained microbial processing of
785 allochthonous organic carbon in boreal lake sediments, Limnol Oceanogr, 57, 163–175, https://doi.org/10.4319/lo.2012.57.1.0163, 2012.

Guggenberger, G. and Zech, W.: Dissolved organic carbon control in acid forest soils of the Fichtelgebirge (Germany) as revealed by distribution patterns and structural composition analyses, Geoderma, 59, 109–129, https://doi.org/10.1016/0016-7061(93)90065-s, 1993.

790 Guggenberger, G. and Zech, W.: Composition and dynamics of dissolved carbohydrates and lignin-degradation products in two coniferous forests, N.E. Bavaria, Germany, Soil Biology Biochem, 26, 19–27, https://doi.org/10.1016/0038-0717(94)90191-0, 2002.

Haei, M., Öquist, M. G., Ilstedt, U., and Laudon, H.: The influence of soil frost on the quality of dissolved organic carbon in a boreal forest soil: combining field and laboratory experiments, Biogeochemistry, 107, 95–
795 106, https://doi.org/10.1007/s10533-010-9534-2, 2010.

Haei, M., Öquist, M. G., Kreyling, J., Ilstedt, U., and Laudon, H.: Winter climate controls soil carbon dynamics during summer in boreal forests, Environmental Research Letters, 8, https://doi.org/10.1088/1748-9326/8/2/024017, 2013.

Hansson, K., Kleja, D. B., Kalbitz, K., and Larsson, H.: Amounts of carbon mineralised and leached as DOC
800 during decomposition of Norway spruce needles and fine roots, Soil Biology Biochem, 42, 178–185, https://doi.org/10.1016/j.soilbio.2009.10.013, 2010.

Heijden, M. G. A. van der, Bardgett, R. D., and Straalen, N. M. van: The unseen majority: soil microbes as drivers of plant diversity and productivity in terrestrial ecosystems, Ecology Letters, 11, 296–310, https://doi.org/10.1111/j.1461-0248.2007.01139.x, 2008.

805   Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnology and Oceanography, 53, 955–969, 2008.

Hensgens, G., Laudon, H., Peichl, M., Gil, I. A., Zhou, Q., and Berggren, M.: The role of the understory in litter DOC and nutrient leaching in boreal forests, Biogeochemistry, 149, 87–103, https://doi.org/10.1007/s10533-
810   020-00668-5, 2020.

Hilli, S., Stark, S., and Derome, J.: Carbon Quality and Stocks in Organic Horizons in Boreal Forest Soils, Ecosystems, 11, 270–282, https://doi.org/10.1007/s10021-007-9121-0, 2008.

Huntington, T. G., Balch, W. M., Aiken, G. R., Sheffield, J., Luo, L., Roesler, C. S., and Camill, P.: Climate change and dissolved organic carbon export to the Gulf of Maine, Journal of Geophysical Research-
815   Biogeosciences, vol. 121, 121, 2700–2716, https://doi.org/10.1002/2015jg003314, 2016.

Jaffé, R., McKnight, D., Maie, N., Cory, R., McDowell, W. H., and Campbell, J. L.: Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties, Journal of Geophysical Research, 113, https://doi.org/10.1029/2008jg000683, 2008.

Jansen, B., Kalbitz, K., and McDOWELL, W. H.: Dissolved Organic Matter: Linking Soils and Aquatic
820   Systems, Vadose Zone Journal, 13, https://doi.org/10.2136/vzj2014.05.0051, 2014.

Jones, D. L. and Kielland, K.: Amino acid, peptide and protein mineralization dynamics in a taiga forest soil, Soil Biology Biochem, 55, 60–69, https://doi.org/10.1016/j.soilbio.2012.06.005, 2012.

Kaiser, K. and Guggenberger, G.: The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils, Org Geochem, 31, 711–725, https://doi.org/10.1016/s0146-6380(00)00046-2, 2000.

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

Kaiser, K., Guggenberger, G., Haumaier, L., and Zech, W.: Seasonal variations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of old-growth Scots pine (Pinus sylvestris L.) and European beech (Fagus sylvatica L.) stands in northeastern Bavaria, Germany, Biogeochemistry, 55, 103–
830   143, https://doi.org/10.1023/a:1010694032121, 2001.

Kalbitz, K.: Changes in properties of soil-derived dissolved organic matter induced by biodegradation, Soil Biology and Biochemistry, 35, 1129–1142, https://doi.org/10.1016/s0038-0717(03)00165-2, 2003.

Kalbitz, K., Meyer, A., Yang, R., and Gerstberger, P.: Response of dissolved organic matter in the forest floor to long-term manipulation of litter and throughfall inputs, Biogeochemistry, 86, 301–318, https://doi.org/10.1007/s10533-007-9161-8, 2007.

835

Kassambara, A. and Mundt, F.: Package "factoextra": Extract and Visualize the Results of Multivariate Data Analyses, https://cran.r-project.org/web/packages/factoextra/, 2017.

Kellerman, A. M., Kothawala, D. N., Dittmar, T., and Tranvik, L. J.: Persistence of dissolved organic matter in lakes related to its molecular characteristics, Nature Geoscience, 8, 454–457, https://doi.org/10.1038/ngeo2440, 840 2015.

Kielland, K., McFarland, J. W., Ruess, R. W., and Olson, K.: Rapid Cycling of Organic Nitrogen in Taiga Forest Ecosystems, Ecosystems, 10, 360–368, https://doi.org/10.1007/s10021-007-9037-8, 2007.

Kirschbaum, M.: The Temperature-Dependence of Soil Organic-Matter Decomposition, and the Effect of Global Warming on Soil Organic-C Storage, Soil Biology and Biochemistry, 27, 753–760, 845 https://doi.org/10.1016/0038-0717(94)00242-s, 1995.

Klotzbücher, T., Kaiser, K., Filley, T. R., and Kalbitz, K.: Processes controlling the production of aromatic water-soluble organic matter during litter decomposition, Soil Biology Biochem, 67, 133–139, https://doi.org/10.1016/j.soilbio.2013.08.003, 2013.

Köhler, S. J., Kothawala, D., Futter, M. N., Liungman, O., and Tranvik, L.: In-lake processes offset increased 850 terrestrial inputs of dissolved organic carbon and color to lakes., PLoS ONE, 8, e70598, https://doi.org/10.1371/journal.pone.0070598, 2013.

Kothawala, D. N., Moore, T. R., and Hendershot, W. H.: Adsorption of dissolved organic carbon to mineral soils: A comparison of four isotherm approaches, Geoderma, 148, 43–50, https://doi.org/10.1016/j.geoderma.2008.09.004, 2008.

855 Kothawala, D. N., Stedmon, C. A., Müller, R. A., Weyhenmeyer, G. A., Köhler, S. J., and Tranvik, L. J.: Controls of dissolved organic matter quality: evidence from a large-scale boreal lake survey, Global Change Biol, 20, 1101–1114, https://doi.org/10.1111/gcb.12488, 2014.

Kreutzweiser, D. P., Hazlett, P. W., and Gunn, J. M.: Logging impacts on the biogeochemistry of boreal forest soils and nutrient export to aquatic systems: A review, Environ Rev, 16, 157–179, https://doi.org/10.1139/a08-860 006, 2008.

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

Lee, M.-H., Park, J.-H., and Matzner, E.: Sustained production of dissolved organic carbon and nitrogen in forest floors during continuous leaching, Geoderma, 310, 163–169, https://doi.org/10.1016/j.geoderma.2017.07.027, 2018.

Lenth, R. V.: Package "lsmeans": Least-squares means, Journal of Statistical Software, 69, 1–33, https://doi.org/10.18637/jss.v069.i01, 2016.

Lilienfein, J., Qualls, R. G., Uselman, S. M., and Bridgham, S. D.: Adsorption of dissolved organic carbon and nitrogen in soils of a weathering chronosequence, Soil Science Society of America Journal, 68, 292–305, 2004.

Malcolm, R. L.: The uniqueness of humic substances in each of soil, stream and marine environments, Anal Chim Acta, 232, 19–30, https://doi.org/10.1016/s0003-2670(00)81222-2, 1990.

Mangiafico, S.S.: Summary and Analysis of Extension Program Evaluation in R, version 1.20.01. rcompanion.org/handbook/. https://rcompanion.org/handbook/I_09.html, 2016.

Marschner, B. and Kalbitz, K.: Controls of bioavailability and biodegradability of dissolved organic matter in soils, Geoderma, vol. 113, 113, 211–235, https://doi.org/10.1016/s0016-7061(02)00362-2, 2003.

McDowell, N. G., Bowling, D. R., Schauer, A., Irvine, J., Bond, B. J., Law, B. E., and Ehleringer, J. R.: Associations between carbon isotope ratios of ecosystem respiration, water availability and canopy conductance: carbon isotope ratio of ecosystem respiration, Global Change Biol, 10, 1767–1784, https://doi.org/10.1111/j.1365-2486.2004.00837.x, 2004.

McDowell, W. H. and Likens, G. E.: Origin, Composition, and Flux of Dissolved Organic Carbon in the Hubbard Brook Valley, Ecol Monogr, 58, 177–195, https://doi.org/10.2307/2937024, 1988.

McGroddy, M. E., Baisden, W. T., and Hedin, L. O.: Stoichiometry of hydrological C, N, and P losses across climate and geology: An environmental matrix approach across New Zealand primary forests, Global Biogeochemical Cycles, 22, https://doi.org/10.1029/2007gb003005, 2008.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T.: Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol Oceanogr, 46, 38–48, https://doi.org/10.4319/lo.2001.46.1.0038, 2001.

Mellander, P.-E., Löfvenius, M. O., and Laudon, H.: Climate change impact on snow and soil temperature in boreal Scots pine stands, Climatic Change, 85, 179–193, https://doi.org/10.1007/s10584-007-9254-3, 2007.

Michalzik, B. and Matzner, E.: Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem: Dynamics of dissolved organic nitrogen and carbon in soil, Eur J Soil Sci, 50, 579–590, https://doi.org/10.1046/j.1365-2389.1999.00267.x, 1999.

Michalzik, B., Kalbitz, K., Park, J. H., Solinger, S., and Matzner, E.: Fluxes and concentrations of dissolved
organic carbon and nitrogen – a synthesis for temperate forests, Biogeochemistry, 52, 173–205,
https://doi.org/10.1023/a:1006441620810, 2001.

Michel, K. and Matzner, E.: Release of dissolved organic carbon and nitrogen from forest floors in relation to
solid phase properties, respiration and N-mineralization, J Plant Nutr Soil Sc, 162, 645–652,
https://doi.org/10.1002/(sici)1522-2624(199912)162:6<645::aid-jpln645>3.0.co;2-t, 1999.

Moore, T. R., Paré, D., and Boutin, R.: Production of Dissolved Organic Carbon in Canadian Forest Soils,
Ecosystems, 11, 740–751, https://doi.org/10.1007/s10021-008-9156-x, 2008.

Näsholm, T., Ekblad, A., NORDIN, A., Giesler, R., Högberg, M., and Högberg, P.: Boreal forest plants take up
organic nitrogen, Nature, 392, 914–916, https://doi.org/10.1038/31921, 1998.

Neff, J. C., Chapin, F. S., and Vitousek, P. M.: Breaks in the cycle: dissolved organic nitrogen in terrestrial
ecosystems, Front Ecol Environ, 1, 205–211, https://doi.org/10.1890/1540-
9295(2003)001[0205:bitcdo]2.0.co;2, 2003.

Oades, J. M.: The retention of organic matter in soils, Biogeochemistry, vol. 5, 5, 35–70,
https://doi.org/10.1007/bf02180317, 1988.

Patel, K. F., Tatariw, C., MacRae, J. D., Ohno, T., Nelson, S. J., and Fernandez, I. J.: Soil carbon and nitrogen
responses to snow removal and concrete frost in a northern coniferous forest, Can J Soil Sci, 98, 436–447,
https://doi.org/10.1139/cjss-2017-0132, 2018.

Patrick, M. E., Young, C. T., Zimmerman, A. R., and Ziegler, S. E.: Mineralogic controls are harbingers of
hydrological controls on soil organic matter content in warmer boreal forests, Geoderma, 425, 116059,
https://doi.org/10.1016/j.geoderma.2022.116059, 2022.

Philben, M., Butler, S., Billings, S. A., Benner, R., Edwards, K. A., and Ziegler, S. E.: Biochemical and
structural controls on the decomposition dynamics of boreal upland forest moss tissues, Biogeosciences, vol. 15,
15, 6731–6746, https://doi.org/10.5194/bg-15-6731-2018, 2018.

Pinheiro, J., Bates, D., and Team, R. C.: Package "nlme": Linear and Nonlinear Mixed Effects Models, 2022.

Poulin, B. A., Ryan, J. N., and Aiken, G. R.: Effects of Iron on Optical Properties of Dissolved Organic Matter,
Environmental Science & Technology, 140813125613009, https://doi.org/10.1021/es502670r, 2014.

Prijac, A., Gandois, L., Jeanneau, L., Taillardat, P., and Garneau, M.: Dissolved organic matter concentration
and composition discontinuity at the peat–pool interface in a boreal peatland, Biogeosciences, vol. 19, 19, 4571–
4588, https://doi.org/10.5194/bg-19-4571-2022, 2022.

Qualls, R. G. and Haines, B. L.: Geochemistry of Dissolved Organic Nutrients in Water Percolating through a
925 Forest Ecosystem, Soil Sci Soc Am J, 55, 1112–1123,
https://doi.org/10.2136/sssaj1991.03615995005500040036x, 1991.

Quinn, G. P. and Keough, M. J.: Experimental Design and Data Analysis for Biologists,
https://doi.org/10.1017/cbo9780511806384, 2002.

Radulovich, R. and Sollins, P.: Improved Performance of Zero-Tension Lysimeters, Soil Sci Soc Am J, 51,
930 1386–1388, https://doi.org/10.2136/sssaj1987.03615995005100050054x, 1987.

Roulet, N. and Moore, T. R.: Environmental chemistry: browning the waters., Nature, 444, 283–284,
https://doi.org/10.1038/444283a, 2006.

Schimel, J. P. and Bennett, J.: Nitrogen mineralization: challenges of a changing paradigm, Ecology, 85, 591–
602, https://doi.org/10.1890/03-8002, 2008.

935 Schimel, J. P. and Clein, J. S.: Microbial response to freeze-thaw cycles in tundra and taiga soils, Soil Biology
Biochem, 28, 1061–1066, https://doi.org/10.1016/0038-0717(96)00083-1, 1996.

Shen, Y., Chapelle, F. H., Strom, E. W., and Benner, R.: Origins and bioavailability of dissolved organic matter
in groundwater, Biogeochemistry, 122, 61–78, https://doi.org/10.1007/s10533-014-0029-4, 2014.

Slessarev, E. W., Chadwick, O. A., Sokol, N. W., Nuccio, E. E., and Pett-Ridge, J.: Rock weathering controls
940 the potential for soil carbon storage at a continental scale, Biogeochemistry, vol. 157, 157, 1–13,
https://doi.org/10.1007/s10533-021-00859-8, 2022.

Soil Classification Working Group: The Canadian System of Soil Classification, 3rd ed., Agriculture and Agri-
Food Canada Publication 1646, 187 pp., ISBN 0-660-17404-9, 1998.

Stark, S., Martz, F., Ovaskainen, A., Vuosku, J., Männistö, M. K., and Rautio, P.: Ice-on-snow and compacted
945 and absent snowpack exert contrasting effects on soil carbon cycling in a northern boreal forest, Soil Biology
Biochem, 150, 107983, https://doi.org/10.1016/j.soilbio.2020.107983, 2020.

Ste-Marie, C. and Paré, D.: Soil, pH and N availability effects on net nitrification in the forest floors of a range
of boreal forest stands, Soil Biology Biochem, 31, 1579–1589, https://doi.org/10.1016/s0038-0717(99)00086-3,
1999.

950 Stevenson, F. J.: Humus Chemistry: Genesis, Composition, Reactions, Second Edition, J Chem Educ, vol. 72,
72, A93, https://doi.org/10.1021/ed072pa93.6, 1995.

Sturm, M., Taras, B., Liston, G. E., Derksen, C., Jonas, T., and Lea, J.: Estimating Snow Water Equivalent
Using Snow Depth Data and Climate Classes, J Hydrometeorol, 11, 1380–1394,
https://doi.org/10.1175/2010jhm1202.1, 2010.

955   Tang, Y., Horikoshi, M., and Li, W.: Package "ggfortify": Unified interface to visualize statistical results of popular r packages, R Journal, 8, 478–489, https://doi.org/10.32614/rj-2016-060, 2016.

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

960   Titus, B. D., Kingston, D. G. O., Pitt, C. M., and Mahendrappa, M. K.: A lysimeter system for monitoring soil solution chemistry, Can J Soil Sci, 80, 219–226, https://doi.org/10.4141/s99-018, 2000.

Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M., and Hendricks, D. M.: Mineral control of soil organic carbon storage and turnover, Nature, 389, 170–173, https://doi.org/10.1038/38260, 1997.

Wachenfeldt, E. von, Sobek, S., Bastviken, D., and Tranvik, L. J.: Linking allochthonous dissolved organic
965   matter and boreal lake sediment carbon sequestration: The role of light-mediated flocculation, Limnol Oceanogr, 53, 2416–2426, https://doi.org/10.4319/lo.2008.53.6.2416, 2008.

Wachenfeldt, E. von, Bastviken, D., and Tranvika, L. J.: Microbially induced flocculation of allochthonous dissolved organic carbon in lakes, Limnol Oceanogr, 54, 1811–1818, https://doi.org/10.4319/lo.2009.54.5.1811, 2009.

970   Weintraub, M. N., Scott-Denton, L. E., Schmidt, S. K., and Monson, R. K.: The effects of tree rhizodeposition on soil exoenzyme activity, dissolved organic carbon, and nutrient availability in a subalpine forest ecosystem., Oecologia, 154, 327–38, https://doi.org/10.1007/s00442-007-0804-1, 2006.

Weyhenmeyer, G. A., Prairie, Y. T., and Tranvik, L. J.: Browning of boreal freshwaters coupled to carbon-iron interactions along the aquatic continuum., PLoS ONE, 9, e88104, https://doi.org/10.1371/journal.pone.0088104,
975   2014.

Žifčáková, L., Větrovský, T., Lombard, V., Henrissat, B., Howe, A., and Baldrian, P.: Feed in summer, rest in winter: microbial carbon utilization in forest topsoil., Microbiome, 5, 122, https://doi.org/10.1186/s40168-017-0340-0, 2017.

980