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

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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% 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.

1 Introduction

Boreal forests occupy 11 % 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% 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% 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 & 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 stands relative to silver birch stands (Fröberg et al., 2011). It is likely that a combination of hydrological and biogeochemical factors regulate DOC production and mobilization through soil, but the

5 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 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

10 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

15 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 ($\sim$ 1000mm yr^{-1}) and is snow-covered for approximately $1/3^{rd}$ 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 facilate a process based

20 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 Materials and Methods

2.1 Site Description

25 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. (lat. 48° 53'14", long. 63° 24' 8"). The site consists of 2 hectares divided into eight 50 x 50 m plots (note: only six were used in this study; Figure 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

30 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 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 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 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 samplewas 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).

2.3 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 (lat. 49° 13' 00" N, long. 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 24th and August 29th, 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 and 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 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 1).

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 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)   (Brakensiek and Rawls, 1994)

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

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 4).

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).

2.6 Soil Temperature and Moisture

Three soil temperature and moisture probes per plot type (Decagon ECH$_2$O -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 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 (Fig. 2C; Table 1).

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 Hydro-Sense 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.

2.8 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 1, Table S1, Fig. 2; *asterisks*). A repeated measures linear mixed effects (RM-LME) model using the 'nlme' package 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 (Fig. 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 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) 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.

3 Results

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 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 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 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 1).

3.2 Soil Respiration

The temporal range in instantaneous CO_2 efflux rates during the lysimeter measurement period (July 2013 – July 2014; Fig. 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).

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 of rainfall, Fig. 1; *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 1, Fig. 2B; 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 (Fig. 2B). The snowpack persisted throughout 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 (Fig. 2A; *snowpack*).

The O and mineral horizons were consistently wetter in harvested plots relative to the forest plots over the duration of the study (Fig. 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 1). The O horizons experienced long periods of drying in the summer, especially in July 2013 (Fig. 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.

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 (Fig. 2A) 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; Fig 2D). Intra-annual variation in DOC concentration was correlated to soil temperature (positive correlation; Table 3) and water flux variation (negative correlation; Table 3) in both plot types. The DOC concentration was negatively correlated to soil moisture in the harvested plots only.

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 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 1).

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 (Fig. 2b; 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 O horizon of harvested plots (Fig. 2c, 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 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 (Fig. 1D,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 (Fig. 1B,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 (Fig. 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 2A) and there was a strong positive correlation between water input and both soil water and DOC fluxes measured in both plot types (Table 2C). There was an interaction between season and water input on DOC fluxes (Table 3), where a linear relationship between water input and DOC fluxes was observed in the summer (Fig. 4A), but DOC fluxes exhibited a tapering off in autumn and snowmelt when water input to soil was high (Fig. 4B,C).

4 Discussion

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 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 patterns (Fig. 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 3). 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

5   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 & Kalbitz, 2012). Vertically-dominated O to mineral horizon DOC fluxes may occur in some boreal systems and they may be relevant at larger spatial

10 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 4), combined with continuous field measurements of O horizon soil moisture, indicate that

15 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 5). At soil moisture contents above matric saturation, capillary 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

20 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

25 (Beven and German, 1982 & 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.

30 **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 (Fig. 4; Table 3). Soils of both plot types appeared to be flushed of DOC during periods of high, continual leaching and

low temperatures (Fig. 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 (Fig 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 (Fig 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 3A), 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.

4.2.1 Water Limited Scenarios: Summer and Winter

Fluxes of water and DOC were dynamic on the weekly to monthly scale during all seasons except winter (Fig 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 3B), 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 (Fig. 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.

4.2.2 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.

4.3 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.

Data availability. All data are included in the paper tables and the Supplement.

Supplement. The supplement related to this article is available online at:

5   *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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Table 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[5] 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

Table 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.

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

Table 3. Two-way ANOVA results examining the effect of water input, season and the interaction on DOC fluxes. Data plotted in Figure 3

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**

Table 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.
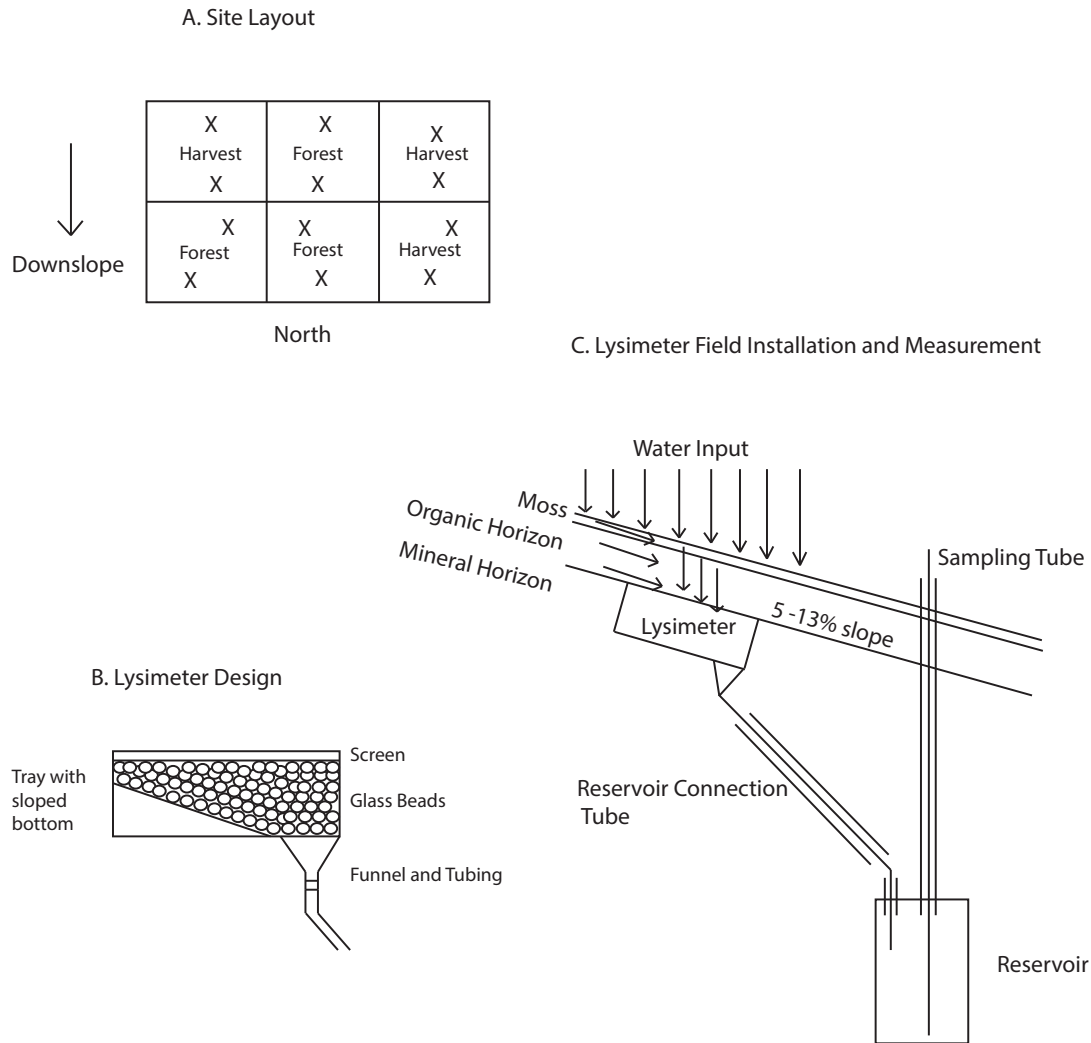
Figure 1. Pynn's Brook Experimental Forest Experimental Design. A north facing black spruce hillslop site divided into 6 50x50m plots, half of which were randomly selected for harvest 10 years prior to lysimeter installation (A). Each plot contains two lysimeter pairs ("X") for a total of 12 harvest 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 infiltrated vertically and laterally through moss and organic layers and into a 25 L reservoir from which samples were retrieved (C).

Figure 2. Temporal variation of 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).

p = 0.0903   p = 0.0084   p = 0.0337
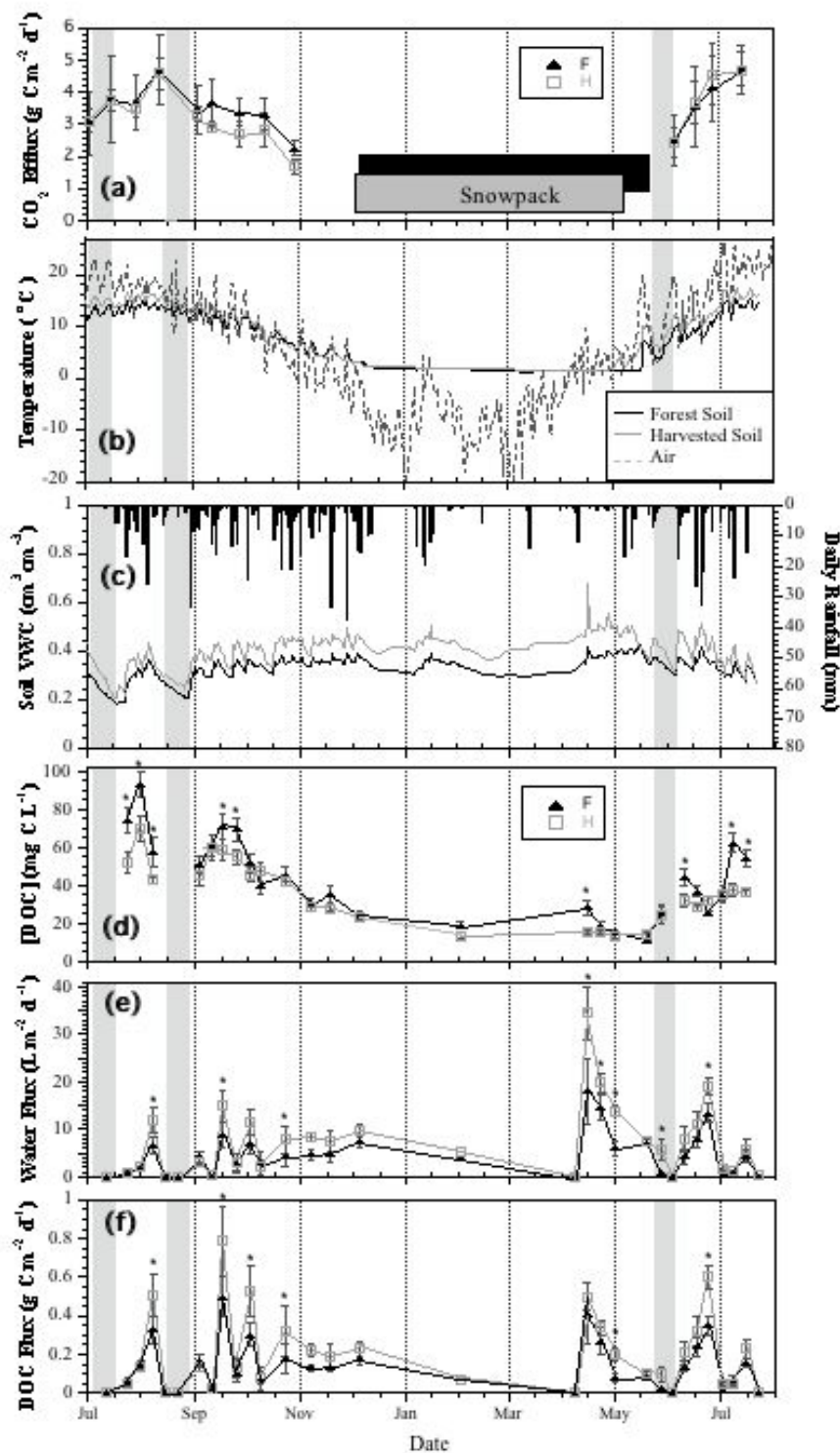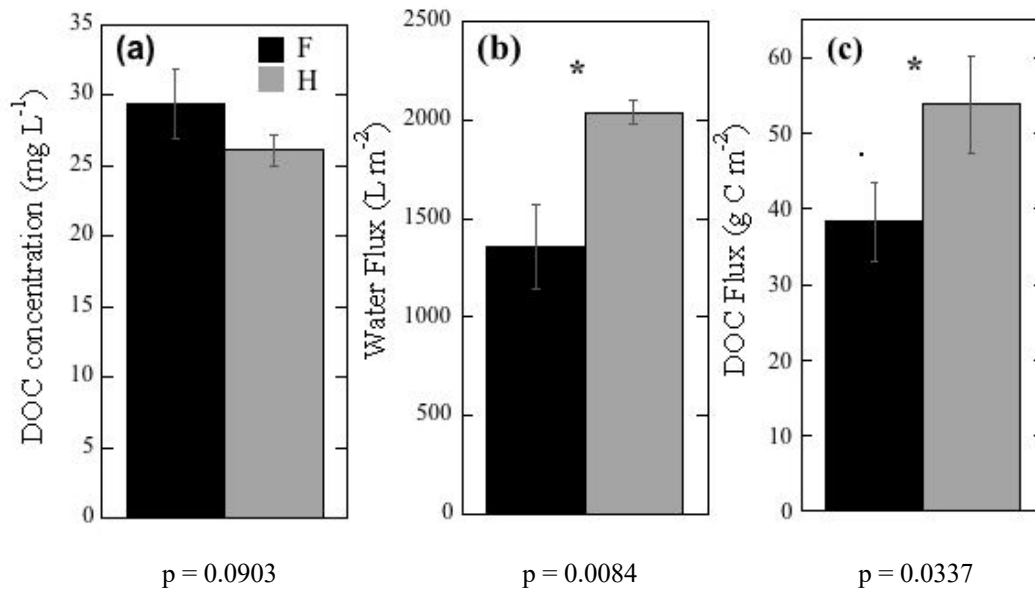
Figure 3. Mean annual lysimeter collected variables. Volume weighted dissolved organic carbon (DOC) concentration (A), total water flux (B), and total DOC flux collected from organic horizons of forest (F) and harvested (H) plots over the entire study period. Annual values were calculated from the accumulated 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).
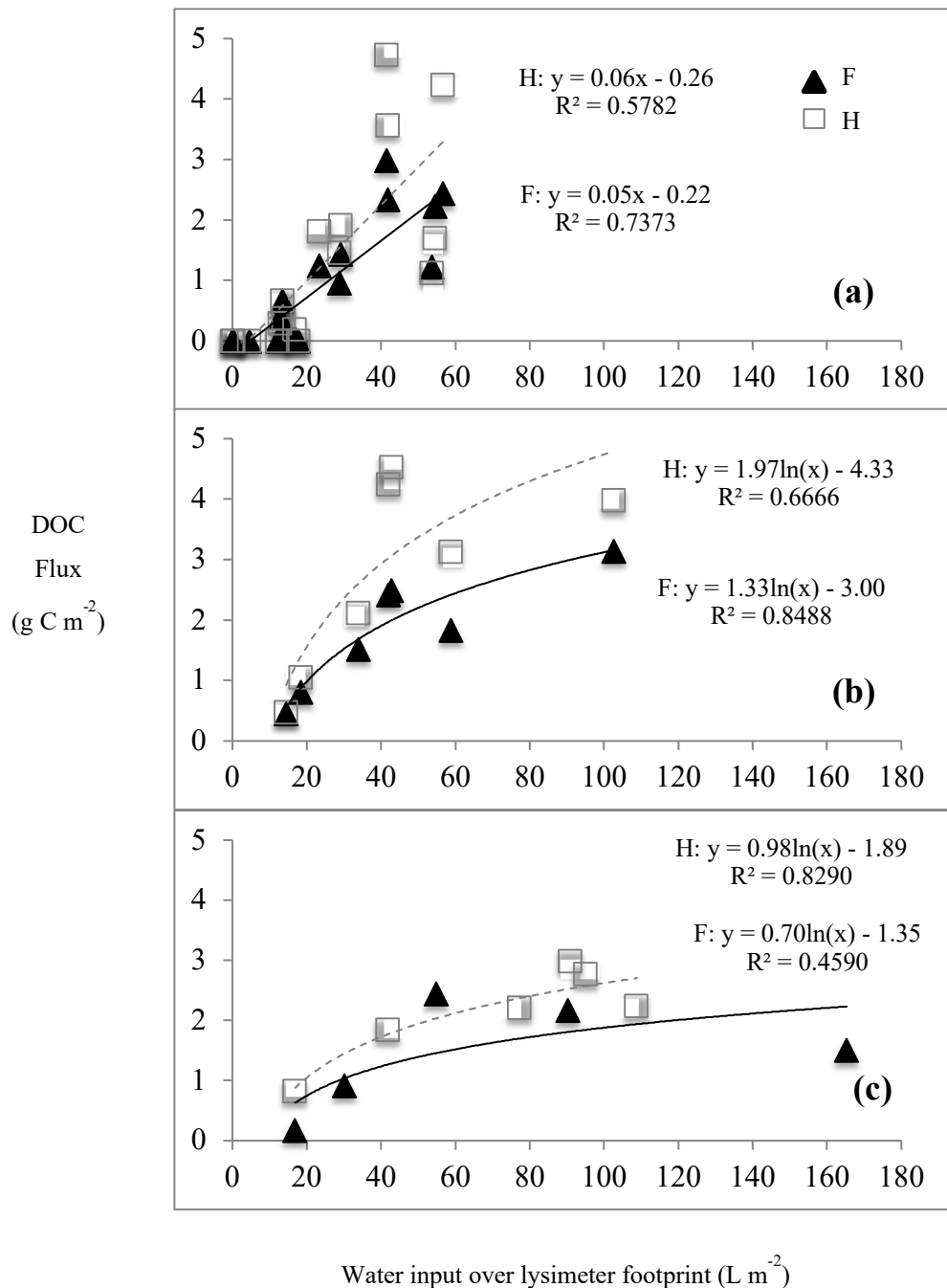
Figure 4. Seasonal relationship between dissolved organic carbon (DOC) fluxes and water input to the soil in mature forest (F) and harvested (H) plots. Seasons are designated as summer (a), autumn (b) and winter + snowmelt (c).
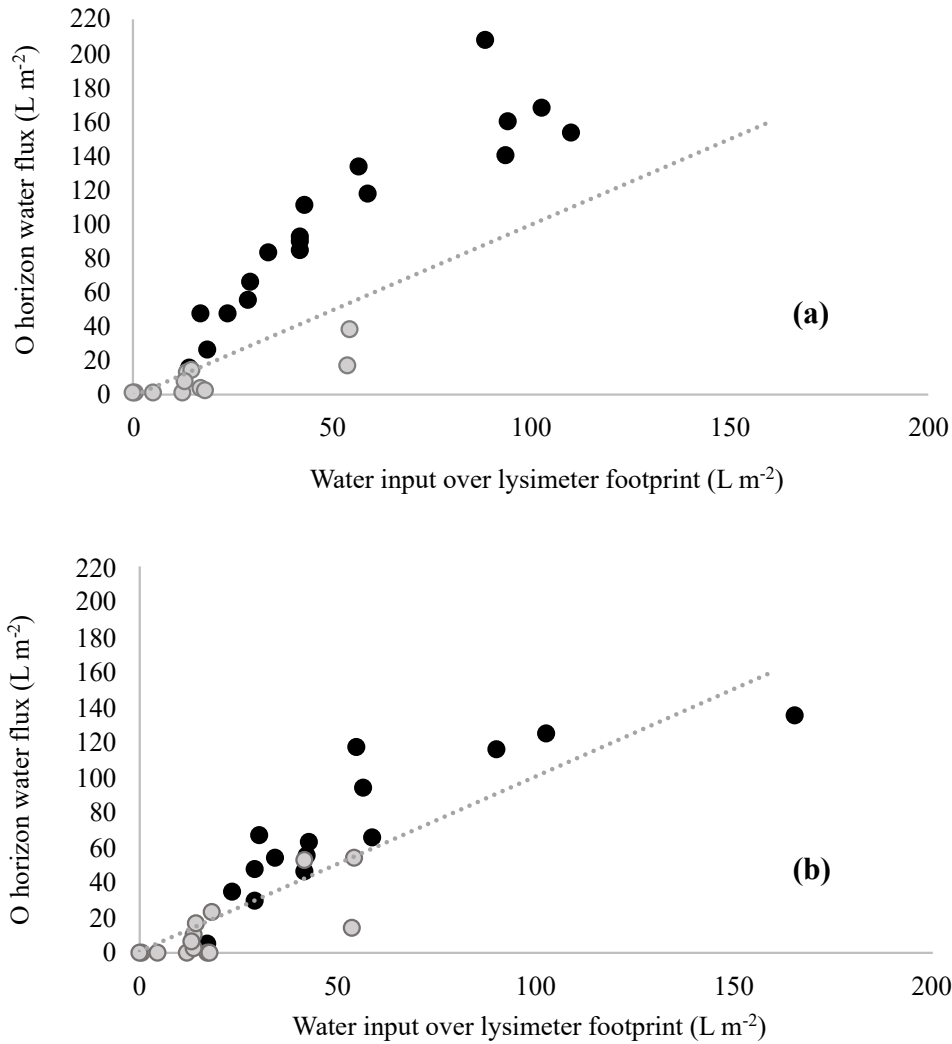
Figure 5. Lysimeter Captured Water Fluxes versus Water Input over the Lysimeter Footprint in harvested (a) and forest (b) plots. Lysimeter collections made during periods when volumetric soil water content remained below soil matrix saturation (grey circles) contrast with lysimeter collections made during 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 evaportation measurements (see Table 4).