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Seasonal Trends of DOM Character in Soils and Stream Change With Snowmelt Timing

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Key Points:

- Differences in snowpack duration influenced the source of dissolved organic matter (DOM) and its character in the stream of the same watershed
- The character of stream DOM was correlated with that of DOM in soil water from north facing aspects within the watershed
- Fluorescence index peak ratio C/A was able to distinguish DOM from different sources along a leaf leachate-soil-stream continuum

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract

In many watersheds, runoff occurring with snowmelt brings the largest pulse of dissolved organic matter (DOM) from soils to streams. Yet, exactly how soil and stream DOM fractions are altered as snowmelt timing changes is not well understood. We studied the optical character of DOM as it moved through a first-order northern hardwood watershed through the snowmelt period. While stream dissolved organic carbon (DOC; mean = 4.6 mg C L^{-1}) concentrations were not correlated with snowmelt flushing, stream DOM appeared humic-like throughout the study period (humification index, HIX; mean = 10.9). Within the stream, we measured seasonal increases in an inverse index of DOM molecular weight and processing (spectral slope, $S_{275-295}$; range = 0.0102–0.0214) and in an index of recently derived DOM (Biological Index, BIX; range = 0.2–1.1). We measured a decrease in an inverse index of DOM oxidation (ratio of Peak C to Peak A, or C/A; range = 0.59–2.01) through the snowmelt period. Stream BIX and C/A tracked those measured in the north aspect soils throughout the study. C/A was unique as it decreased from source to stream, likely reflecting the diagenesis of DOM through soils. These data suggest that changes in the timing of snowmelt and hydrologic connectedness within a watershed affect seasonal changes in stream DOM character. We suggest that watersheds with deep glacial till parent materials have stream connectivity limited by subsurface flow paths, with stream DOM character being determined largely by slow melt and a longer period of infiltration.

1. Introduction

Dissolved organic matter (DOM) represents a major and mobile carbon pool in the Earth's carbon cycle (Battin et al., 2009). Terrestrial DOM is one of the largest sources of organic carbon delivered to aquatic ecosystems (Tranvik et al., 2009), and the passage of terrestrial DOM within and through soils on its path to streams is complex (Qualls & Haines, 1992). DOM encompasses a broad continuum of organic materials formed by the degradation and subsequent polymerization of terrestrial and microbial inputs (Stevenson, 1994). Processing by microbes, interactions with reactive minerals, and abiotic degradation as these compounds move into and through soils can have important effects on the composition of DOM delivered to aquatic environments (Hutchins et al., 2017; Kaiser & Kalbitz, 2012).

Infiltration of water translocates DOM through soils (Kaiser & Kalbitz, 2012; Rothstein et al., 2018). In regions where snowmelt is a large contributor to the annual hydrograph, infiltration can be highest during the spring freshet (Stottlemyer & Toczydlowski, 1991), and this often results in the largest flush of DOM from watersheds (e.g., Boyer et al., 1997; Hornberger et al., 1994). The magnitude of water associated with these infiltration pulses determines the ability of terrestrially sourced DOM, such as DOM from fresh leaf litter, to pass into the mineral horizons, with varying degrees of alteration (Rothstein et al., 2018). However, exactly how changes in the timing or amounts of precipitation may affect DOM exports from soils is uncertain.

In snowmelt-dominated systems, warmer winters associated with a changing climate may be counterintuitively accompanied by wetter, colder soils owing to slower, earlier snowmelt and decreased snow cover to insulate the soil (Groffman et al., 2001; Musselman et al., 2017). These factors also affect microbial processes that are important for the solubilization of OM (Fitzhugh et al., 2001; Song et al., 2017). As such, the changes in snowmelt timing predicted to occur in a warmer world (Ashley et al., 2020; Hayhoe et al., 2007) will likely affect the

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degree of infiltration into soils, but there is still much uncertainty as to how these processes will in turn affect the movement and transformation of DOM from soils to streams.

In addition to changes in climate, local differences in snow accumulation largely determine the vertical movement of DOM through infiltration, which in turn influences soil horizon formation in forested watersheds—particularly when underlain by soils with high permeability, such as glacial till (Schaetzl & Isard, 1991, 1996; Schaetzl et al., 2015). For example, the lower incident solar radiation and insolation on polar-facing aspects relative to equatorial-facing aspects leads to a higher degree of infiltration relative to evaporation, which has been shown to alter DOM movement in soils over time (Hunckler & Schaetzl, 1997). In many forested soils developed through illuviation due to infiltration of precipitation (e.g., Spodosols), a fraction of DOM from plant materials such as leaf litter is stabilized in upper mineral soil horizons (Kaiser & Guggenberger, 2000). These processes confine the majority of soil organic matter near the surface in Spodosols, particularly in the litter layer. As such, these soil and litter-derived pools of DOM are likely the main contributions to streams in forested watersheds and therefore bring distinct characteristics to stream DOM (McDowell & Wood, 1984; Qualls & Haines, 1992).

Variability in the input of surface-soil derived DOM to streams can be high depending on snowmelt dynamics (Boyer et al., 2000), and in particular the proportion of water that occurs as surface runoff versus deeper soil flow paths (Ågren et al., 2010; Tiwari et al., 2019). Ground water flow paths have longer residence times than surface runoff, which can result in more DOM processing and mineralization (Laudon et al., 2007). Moreover, periods of high flow, such as occur with peak snow melt or storms, exhibit higher connectedness between soils and stream, and often result in the export of DOM with a more humified character (Ågren et al., 2008; Fellman et al., 2009). It is important to note that much of what is understood about snowmelt controls over DOM export has come from watershed studies where shallow subsurface flow dominates the snowmelt hydrograph, particularly in montane watersheds with shallow bedrock (cf. Boyer et al., 1997, 2000; Creed et al., 2008). While there is an emerging understanding of legacy snowmelt recharge on talus flow (Williams et al., 2015), there is still much uncertainty of how changes in snowmelt patterns affect the amount and character of DOM in flow paths from soils to streams in watersheds underlain with coarse textured deep till soils (but see Agren et al., 2014; Laudon et al., 2013).

The objective of this study was to investigate changes in the character of DOM along continua of formation from leaf litter to different soil horizons, and ultimately its export to a small, first-order stream. Furthermore, we assessed how differences in the timing of snowmelt affected DOM character in the stream throughout the growing season. We measured seasonal trends in DOM from north and south facing aspects with different snowmelt dynamics, which may be similar to those expected with future climate change, and compared these with seasonal trends in stream DOM character. We investigated source material variation in DOM in tree leaf leachates, A and B or E soil horizons and the stream using absorption and fluorescence spectroscopy. We hypothesized that peak DOC concentrations would be associated with peak stream flows during snowmelt. We also expected to see changes in the stream DOM character corresponding with changes in the connectivity of soils and the stream on north versus south aspects, owing to differences in the timing of snowmelt. Specifically, near-surface soil flow paths (0–30 cm) are most relevant to our questions in this watershed, owing to the total pool of organic matter being confined near the surface in Spodosols (Table S1 in Supporting Information S1), with otherwise sandy till extending for tens of meters. In fact, these deep till soils can easily accommodate infiltration from peak snow melt, with antecedent soil moisture conditions—largely influenced by aspect and/or climate changes—determining the transport of solutes (Schaetzl & Isard, 1991, 1996). Our study examined whether variation in snowmelt timing on different aspects within the same watershed affect stream DOM composition and concentration. We hypothesized that the north slope would be more hydrologically connected to the stream, and that the variation in soil DOM on the north aspect would be the largest influence on stream DOM character because of a slower snow melt and wetter soils later in the spring. In this context, we specifically evaluated differences in snowmelt timing between aspects as controls of DOM delivery to the stream.

2. Materials and Methods

2.1. Study Site Characterization

The Brooks Gorge watershed is located 6 km northwest of Michigan Technological University (latitude: 47.1601, longitude: −88.6273) in the Upper Peninsula of Michigan, USA (Figure 1). The region receives an average of 828 mm of precipitation annually (1983–2018; National Atmospheric Deposition Program; MI99), with an average

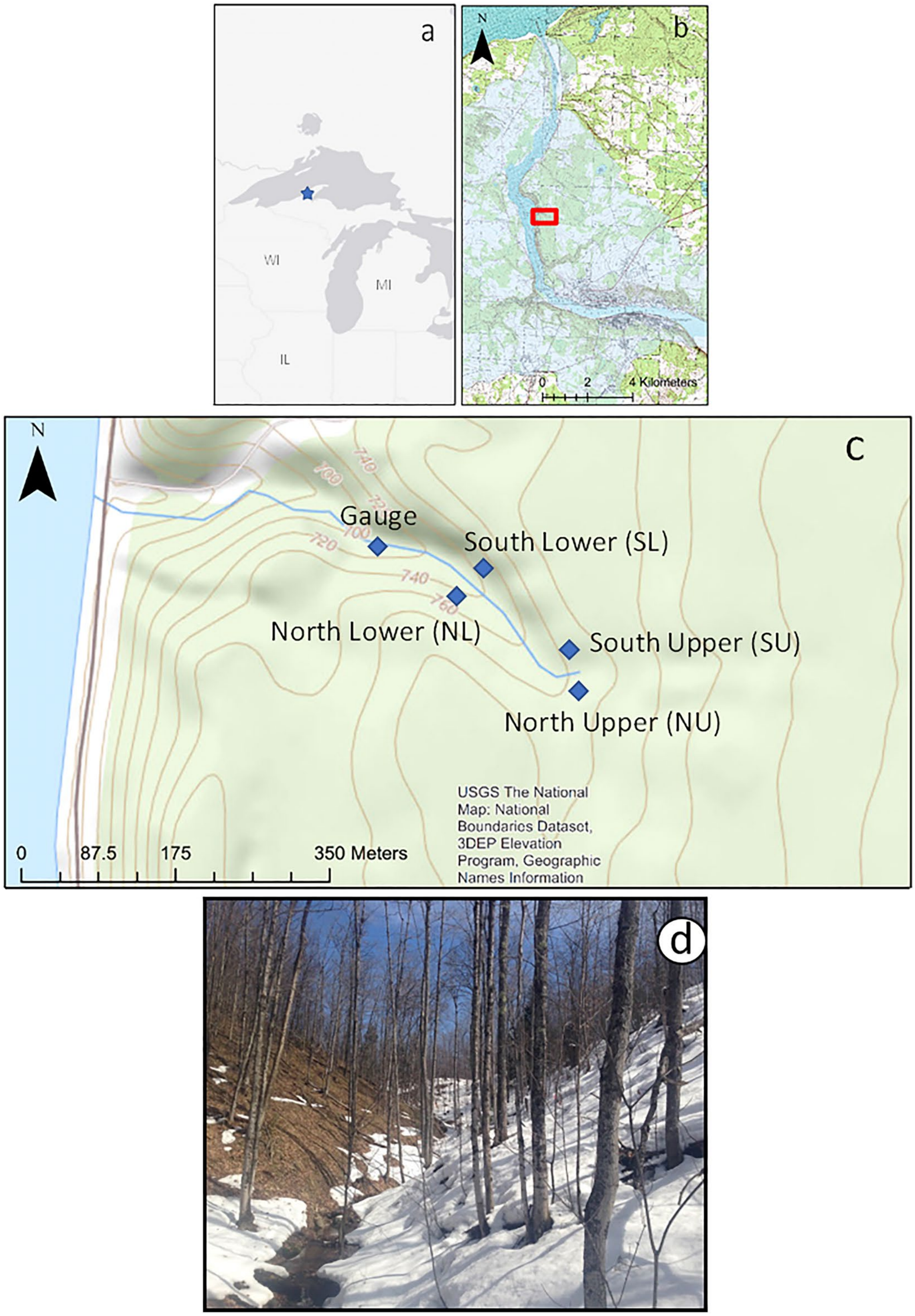

Figure 1. (a) The location of the Brooks Gorge watershed study site in the Upper Peninsula of Michigan. (b) The location of the watershed in relation to the Portage Shipping Canal and Lake Superior (red square in pane (b)). (c) The study site plot layout within the watershed. (d) A photo looking upstream from the middle of the watershed taken on 29 March 2016, highlighting the snowpack differences across aspects. The south facing slope was nearly snow-free while the north facing slope held an average snow depth of 25.7 cm.

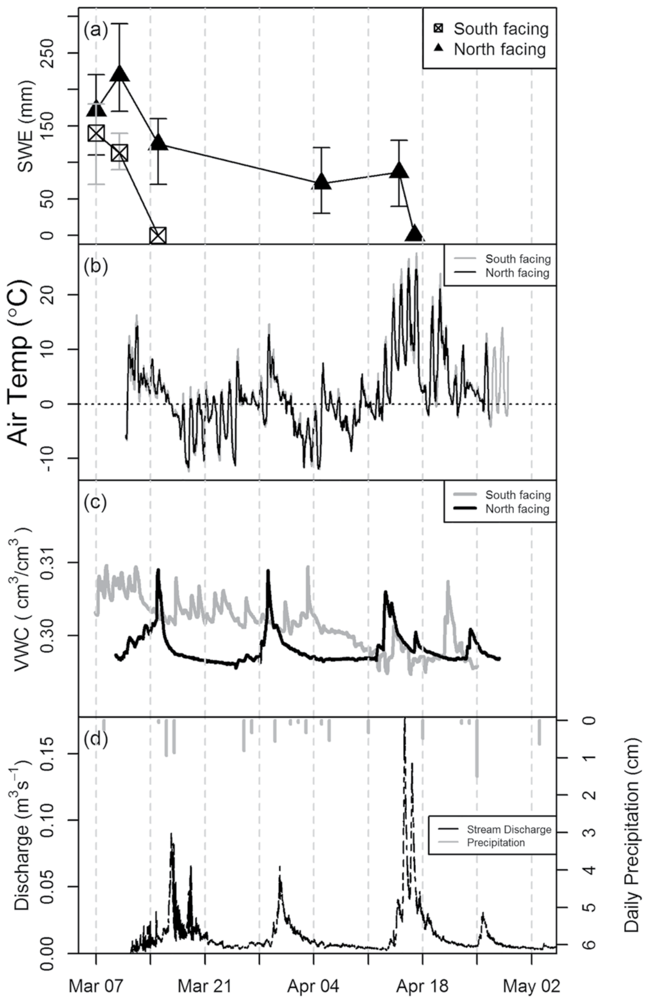

Figure 2. (a) Snow water equivalent (SWE) with the range of five sampling locations represented as error bars, (b) Air temperature and (c) soil volumetric water content (VWC) from north and south facing aspects, and (d) stream discharge and local precipitation over the course of the snowmelt period.

peak snow water equivalent (SWE) of 271 mm (range of 183–444 mm) and mean annual temperature of 4.5°C (Meingast, Kane, et al., 2020). The approximately 20 ha watershed is oriented east to west, causing north to south aspect contrasts (Figure 1), with slopes of about 15% (ranging from 8% in the lower reach to as steep as 70% in the upper reach). The lower portion of the stream (L, Gauge) supports year-round flow, while the upper portion (U) is intermittent. The watershed forest cover is mixed northern hardwoods, dominated by *Acer saccharum* (Marsh.), *Acer rubrum* (L.), *Tilia Americana* (L.), *Betula alleghaniensis* (Britton), *Quercus rubra* (L.) and *Ostrya virginiana* (Mill.). The glacial-till soils are described as a complex of Fragiorthods (Graveraet Series) and Haplorthods (Kalkaska Series), which have sand content >75% (Table S1 in Supporting Information S1). Spodic horizons are more developed on the north facing aspects, with B horizons having average thicknesses of 45 and 29 cm on north and south facing aspects, respectively (Table S1 and Figure S1 in Supporting Information S1).

2.2. Stream and Soil Water Characterization

Stream samples were collected for optical characterization on 27 days, herein defined as "peak runoff", from just prior to melt onset (11 March 2016) to summer baseflow (2 June 2016) at three sampling locations along the reach (upper (U), lower (L), and Gauge) (Figure 1c). Of these 27 days, stream samples were analyzed on 19 days for DOC concentrations. Sampling during the freshet was focused on precipitation events or warming, which has been shown to be effective in capturing export dynamics in small headwater streams in the region (Stottlemyer & Toczydlowski, 2006). Soil pore water was collected for 13 days over the same period using a total of 16 porous cup tension lysimeters with approximately 50 centibars of vacuum applied (Soil Moisture Corporation; Santa Barbara, CA, USA). Two lysimeters were inserted to two depths (15 and 30 cm; chosen to sample lower A horizon and lower B or B/E horizon DOM) on each aspect (North (N) and South (S)) corresponding to the two stream sampling locations (U and L; Figure 2). Lysimeter pairs were located less than 1 m apart and approximately 10 m from the other lysimeter pair in the station. Each station was located at the approximate middle of the hillslope creating a 20–40 m distance to the stream. This design produced four lysimeters per station. Pore water and stream samples were immediately filtered through 0.45 μm PVDF syringe filters into opaque HDPE bottles and transported to the laboratory under refrigeration for spectroscopic analyses within 24 hr. Samples obtained for DOC concentrations were additionally preserved by freezing prior to analysis, which allowed for all samples to be analyzed at one time. While freezing may result in a lower detectable (DOC) concentration, this effect is negligible (0%–3%) in low-carbon (<5 mg DOC L^{-1}) samples (Fellman et al., 2008).

Stream stage was measured from 11 March to 25 May with a Solinst Levellogger 3001 and barometrically corrected with a Solinst Barologger 3001 (Solinst; Georgetown, ON, CA). Stage was converted to volumetric discharge through a rating curve that was developed by collecting all flow at a naturally constrained point in the stream during a timed sample with a 26 L container. This was measured at five times that spanned the range of flow conditions (Brooks et al., 2013; Figure S2 in Supporting Information S1). Soil volumetric water content (VWC) was measured at Lower stations every 30 min using ECH_2O moisture probes (Meter Environment; Pullman, WA, USA). Soil moisture probes were calibrated with gravimetric soil moisture data obtained using fixed-volume corers at the same depths, obtained within 10 m of the stations. Soil moisture data reported are an average of 15 and 30 cm depths, owing to variation in the presence and development of E horizons and spodic horizons. Air temperature was also recorded at Lower stations for both aspects using Onset TMC6-HD temperature sensors recorded with 4-Channel External HOBO loggers at 30 min timesteps (Onset Corporation; Bourne, MA, USA). SWE was measured at each of the four stations using a Federal Snow Sampler six times from peak SWE until each station was snow-free (7 March to 17 April 2016). Five snow cores were collected along 50 m transects at each station for each sampling date. Snow cores were weighed with a Brecknell ElectroSamson scale (Brecknell; Fairmont, MN, USA).

2.3. Leaf Leachates

Recently senesced leaves were collected to establish a fresh DOM endmember signal for the analysis, as previously described in detail (Meingast, Grunert, et al., 2020). Leaves for three species, *Acer saccharum* (Marsh.), *Betula papyrifera* (Marsh.), and *Quercus rubra* (L.) were collected in triplicate, twice in November 2018 after leaf fall. Leaf leachates were created by steeping 5.0 mg of fresh litter in 250 ml of MilliQ water for 4 hr at 4°C (similar to McKnight et al., 1993). Samples were filtered through Whatman 0.7 μm glass fiber filters (Cytiva, Marlborough, MA, USA) followed by Whatman 0.45 μm nylon membrane filters (Cytiva, Marlborough, MA, USA).

2.4. Chemical and Optical Analyses

Absorption and fluorescence spectra of stream samples, soil pore-water samples, and leaf leachates were analyzed using a Horiba Aqualog fluorometer (Horiba-Jobin-Yvon Aqualog C; Horiba Co., Edison, NJ, USA) in 1 cm quartz cells (Starna Cells, Inc., Atascadero, CA, USA). Absorption spectra were run from 240 to 600 nm at 3 nm resolution. Fluorescence spectra were recorded at 3 nm resolution for excitation wavelengths from 240 to 600 nm and emission was recorded at 3 nm resolution from 212 to 640 nm (Figure S3 in Supporting Information S1). Samples with absorbance greater than 0.6 at $\lambda = 254$ were diluted to satisfy the assumption of detector linearity required by modeling (Horiba Corp., 2012). While prior work has suggested a more conservative cutoff of absorbance at 0.3 (Ohno, 2002), a threshold of 0.6 has been deemed appropriate for DOM-rich matrices (Zsolnay, 2002; see Figure 2 in: Miller et al., 2010). Data post-processing and correction for inner filter effects followed Lawaetz and Stedmon (2009) and Stedmon and Bro (2008) as described in detail in Meingast, Grunert, et al. (2020). Fluorescence spectra were converted to Raman units (R.U.) using Raman scattering from a sealed Milli-Q cuvette (Starna Cells, Inc., Atascadero, CA, USA; (Lawaetz & Stedmon, 2009)). Absorbance values were converted to Naperian absorption coefficients (a_λ) (Green & Blough, 1994):

$$a_\lambda = 2.303\frac{A_\lambda}{L} \quad (1)$$

where A_λ is absorbance at wavelength λ, and L is the path-length, in meters. Inner filter effects, Raman scattering, and Raleigh scattering for fluorescence EEMs were accounted for using the PLS toolbox (version 782; Eigenvector) in Matlab (r2014a).

We derived two specific spectral slopes ($S_{275-295}$ and $S_{350-400}$) from the absorption spectra as indicators of average DOM molecular weight (Helms et al., 2008). These were calculated as the slopes of the linear regressions of log-transformed absorption spectra from 275 to 295 and 350–400 nm, respectively.

We also derived three indices from the fluorescence spectra. The biological index (BIX), used to differentiate terrestrial reference standards from phytoplankton derived DOM (Osburn et al., 2019) was defined as follows:

$$\mathrm{BIX} = \frac{F_{380}}{F_{430}} \quad (2)$$

where F_{380} and F_{430} are the fluorescence emission intensities at 380 and 430 nm, respectively, at an excitation wavelength of 310 nm.

We also calculated humification index (HIX), an index of soil humification (Ohno, 2002; Zsolnay et al., 1999), as follows:

$$\mathrm{HIX} = \frac{\Sigma F_{435-480}}{\Sigma F_{300-345}} \quad (3)$$

where $\Sigma F_{435-480}$ is the sum of the fluorescence emission from 435 to 480 nm and $\Sigma F_{300-345}$ is the sum of the fluorescence emission from 300 to 345 nm at an excitation wavelength of 254 nm.

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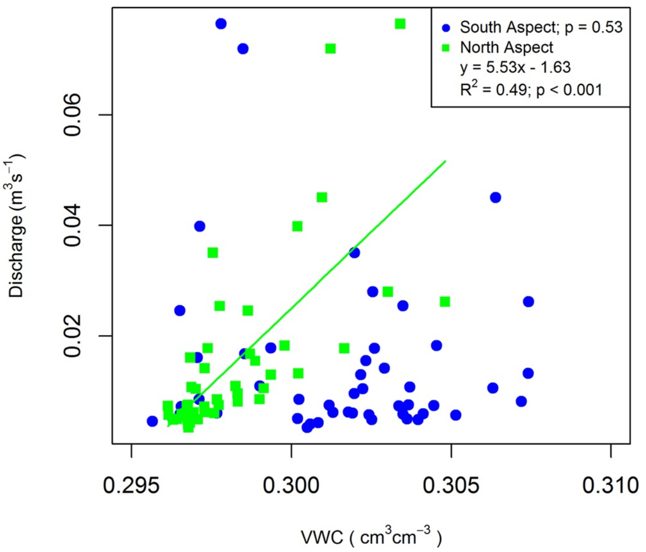

Figure 3. Relationship between average daily soil volumetric water content (VWC) and discharge on north and south facing aspects. North aspect displayed a linear relationship while south aspect displayed no trend between soil VWC and stream discharge.

Additionally, the ratio of fluorescence Peak C to Peak A (C/A), which has been shown to inversely track photodegradation of DOM (Coble, 1996; Hansen et al., 2016) as well as the degree of humic substance degradation or oxidation (Kothawala et al., 2012; Moran et al., 2000) was calculated as follows:

$$C/A = \frac{F_{ex340/em440}}{F_{ex260/em450}} \quad (4)$$

where $F_{ex340/em440}$ is the fluorescence emission at excitation wavelength 340 nm and emission wavelength 440 nm and $F_{ex260/em450}$ is the fluorescence emission at excitation wavelength 260 nm and emission wavelength 450 nm.

All samples were acidified to pH 2 with hydrochloric acid and analyzed for total organic carbon with a Shimadzu TOC-V analyzer (Shimadzu; Kyoto, Japan). We also report the specific absorbance normalized by DOC concentration of the sample ($SUVA_{254}$), which has also been related to DOM aromaticity (Weishaar et al., 2003).

2.5. Statistics

To test differences in DOM character among leaf leachates, soil pore-water, and stream samples, an analysis of variance (ANOVA) with a Tukey's honest significant difference test was used to assess mean differences in absorption and fluorescence indices and DOC concentrations among sampling locations. Linear regression was used with non-parametric Mann Kendall trend analysis to analyze potential trends in stream DOC concentrations, soil moisture, and absorption and fluorescence indices through time in R (v3.0.3; R Core Team, 2014), with results being significant at $\alpha = 0.05$. Linear regressions of daily mean soil VWC and mean daily stream discharge were used to analyze the connectivity between hillslopes on the two aspects and stream over time.

3. Results

3.1. Hydrology

Snowpack measured at the onset of this study (7 March) was similar between north and south aspects (Figure 2a) with mean SWE of 170 and 140 mm on the north and south facing aspects, respectively. The total snowpack melted much more rapidly on the south facing slopes, rendering them snow-free about 1 month before the north slopes (Figure 1d). Air temperatures exhibited a wide range, from −12°C to 28°C on the south-facing aspect and −11°C to 25°C on the north aspect. Both aspects followed similar diurnal trends in temperature (Figure 2b). Soil VWC values measured at the Lower stations ranged from 0.28 to 0.31 $cm^3\ cm^{-3}$. Soil VWC slowly declined over the course of the study period for the south aspect (Mann Kendell trend test; $p < 0.001$) but displayed no overall trend on the north aspect (Mann Kendell trend test; $p = 0.13$; Figure 2c). There were periodic pulses of increased VWC (wetting) in the north aspect soils which were related to stream hydrograph peaks ($R^2 = 0.49$, $p < 0.001$; Figures 2c and 2d; Figure 3). This relationship held true for the north aspect during peak runoff ($R^2 = 0.49$, $p < 0.001$) but not for the south aspect ($R^2 = 0.008$, $p = 0.53$). We note that while the differences in magnitude of our VWC measurements on different aspects approach the reported accuracy of the probes (±3%), the wetting pulses observed only on the north aspect soils (Figure 2c) are well within instrument detection limits. The north aspect soils had snow cover 38 days during peak runoff whereas the south aspect soils were only snow covered 4 days during this period (Figure 2a). Stream discharge peaked at 0.180 $m^3\ s^{-1}$ on 15 April, far exceeding all other streamflow rates during the study period (Figure 2d). This peak corresponded with warming air temperature (Figures 2b and 2d).

3.2. DOC Concentrations

Stream DOC concentrations ranged from 2.3 to 5.9 mg L^{-1}, with a mean of 4.6 mg L^{-1} (Figure 4). There were no significant trends in stream DOC concentration with time nor discharge. Soil lysimeter DOC concentrations ranged

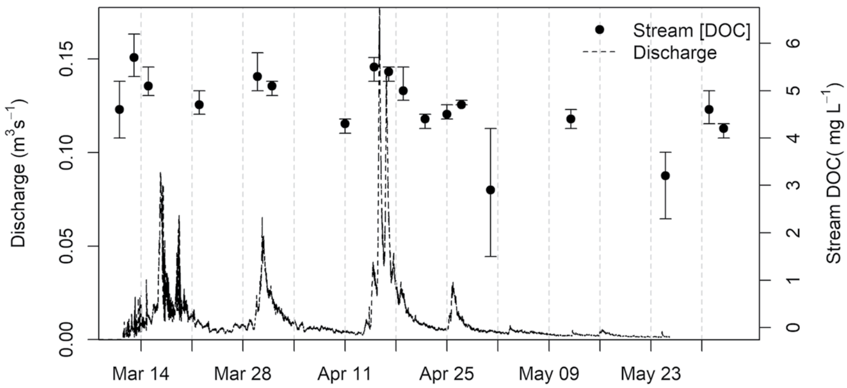

Figure 4. Stream discharge and mean stream dissolved organic carbon (DOC) concentrations over the study period. Vertical bars indicate the range of the three stream sampling locations. Discharge data were collected until 25 May when the well point containing the pressure transducer shifted.

from 11.0 to 79.3 mg L^{-1} (S.E. = 4.5 mg L^{-1}) on the north aspect and from 7.6 to 76.1 mg L^{-1} (S.E. = 4.8 mg L^{-1}) on the south aspect. There was not a significant difference in DOC concentrations between aspects. DOC concentrations did not vary with time across lysimeter locations, or when data were pooled by aspect.

3.3. Absorption Metrics

$SUVA_{254}$, an index of aromaticity, ranged from 0.62 to 4.86 in leaf leachates, with oak being the most aromatic (Meingast, Grunert, et al., 2020). $SUVA_{254}$ ranged from 1.2 to 3.6 in the stream and did not show a significant trend through time. Stream $SUVA_{254}$ was significantly lower than all soil lysimeter locations except north-facing 30 cm lysimeters (Table 1).

$S_{275–295}$, an indicator of average DOM molecular weight, was most variable in leaf leachates, where it ranged from 0.0102 to 0.0200. $S_{275–295}$ ranged from 0.0145 to 0.0189 in the stream, 0.0115 to 0.0154 on the south facing aspect and 0.0118 to 0.0214 on the north facing aspect (Figure 5a). Leaf leachate $S_{275–295}$ values were not statistically different from north facing 15 cm lysimeters, and were significantly higher than all south lysimeter depths and significantly lower than the stream and north facing 30 cm lysimeters (Table 1). $S_{275–295}$ values were significantly lower than the stream values in all soil locations, except for the north facing 30 cm lysimeters (Table 1). There was a significant increase in the stream $S_{275–295}$ through the study period. $S_{275–295}$ showed no trend through time for lysimeters from either aspect (Figure 5a).

$S_{350–400}$, another indicator of average DOM molecular weight, ranged from 0.0139 to 0.0268 in leaf leachates. $S_{350–400}$ ranged from 0.0134 to 0.0590 in the stream, 0.0165 to 0.0363 on the south facing aspect lysimeters and 0.0161 to 0.0407 on the north facing aspect lysimeters (Figure 5b). $S_{350–400}$ was not significantly different between aspects or among sample locations (Table 1) and showed no time trends at any location, though there was an increase on 29 March coincident with a hydrograph peak (Figure 5).

Table 1
Absorption and Fluorescence Indices (Mean and Standard Error) From Leaf Leachates, Soil Lysimeters and Stream Water

Location	$SUVA_{254}$ (L mg C^{-1} m^{-1})	$S_{275–295}$	$S_{350–400}$	HIX	BIX	C/A
Leaf Leachates (n = 18)	2.5(0.3)[a] (n = 18)	0.0147(0.0006)[a]	0.0172(0.0007)[a]	1.0(0.1)[a]	0.39(0.05)[a]	1.38(0.07)[a]
North-facing 15 cm lysimeters (n = 24)	7.1(1.3)[b] (n = 12)	0.0136(0.0003)[a,b]	0.0220(0.0024)[a]	14.6(0.9)[b]	0.48(0.01)[b]	0.75(0.02)[b]
North-facing 30 cm lysimeters (n = 24)	3.6(0.3)[a] (n = 11)	0.0160(0.0003)[c]	0.0214(0.0010)[a]	10.6(1.2)[d]	0.62(0.01)[c]	0.74(0.01)[b]
South-facing 15 cm lysimeters (n = 28)	6.3(1.1)[b] (n = 17)	0.0133(0.0002)[b]	0.0191(0.0003)[a]	19.1(1.3)[c]	0.46(0.01)[a,b]	0.73(0.02)[b]
South-facing 30 cm lysimeters (n = 27)	7.7(1.9)[b] (n = 19)	0.0136(0.0002)[b]	0.0204(0.0009)[a]	17.2(1.0)[b,c]	0.50(0.01)[b]	0.72(0.01)[b,c]
Stream (n = 77)	2.8(0.1)[a] (n = 56)	0.0161(0.0001)[c]	0.0200(0.0007)[a]	10.9(0.2)[d]	0.59(0.03)[c]	0.66(0.004)[c]

Note. Different letters indicate significant differences among locations and depths (α = 0.05). Number of samples (n) for $SUVA_{254}$ is reported as it varied compared to other metrics.

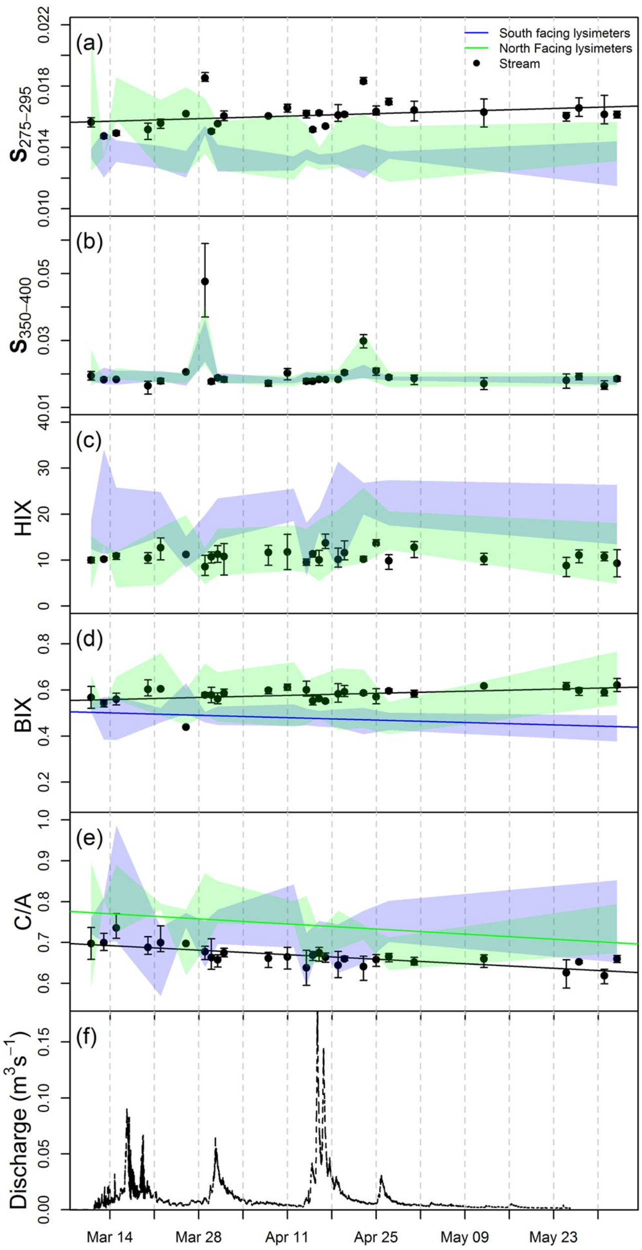

Figure 5. Soil lysimeter and stream absorption and fluorescence metrics through the study period. Regression lines represent significant trends in time. (a) $S_{275–295}$ (Stream Mann-Kendall trend test; $p < 0.01$); (b) $S_{350–400}$; (c) HIX; (d) BIX (Stream Mann-Kendall trend test: $p = 0.02$; South aspect Mann-Kendall trend test: $p < 0.01$); (e) C/A (Stream Mann-Kendall trend test: $p < 0.001$; North aspect Mann-Kendall trend test: $p = 0.02$); Stream sampling locations were averaged as a way to represent the overall character of the stream. Vertical bars indicate the range of the three stream sampling stations. Shaded regions represent the ranges of lysimeter water from north (green shading) and south (blue shading) aspects. (f) Stream discharge over the study period.

3.4. Fluorescence Metrics

HIX, an index of DOM humification, ranged from 0.5 to 2.0 in leaf leachates. HIX ranged from 6.4 to 15.6 in the stream, 6.6 to 34.1 on the south facing aspect and 3.7 to 25.7 on the north facing aspect (Figure 6c). For reference, HIX values can range from 5 to 15 in stream systems, with photodegradation influencing lower values (Wilske et al., 2020) and polymerization leading to higher values (Nguyen et al., 2010), whereas the index can be as high as 40 in soil environments rich in fulvic acids (Ohno, 2002). HIX was similar between north facing 30 cm lysimeters and stream, however, all other lysimeter locations and depths were significantly higher than the stream (Table 1), which was higher than the leaf leachate. Fifteen and 30 cm lysimeters had significantly higher HIX on the south facing aspect than on the north facing aspect, however 30 cm south facing lysimeters were not significantly different from either 15 cm location. There were no time trends in HIX (Figure 5c).

BIX, an index used to indicate autochthonous DOM production (Huguet et al., 2009) and used here as an index of lability or "freshness" (Shatilla & Carey, 2019), ranged from 0.2 to 1.1 in leaf leachates. BIX ranged from 0.5 to 0.6 in the stream, 0.4 to 0.6 on the south-facing aspect and 0.4 to 0.8 on the north-facing aspect (Figure 6d). Similar to HIX, BIX values from north-facing 30 cm lysimeters were similar to the stream while BIX values from all other lysimeter locations were lower (Table 1). The south aspect showed a decrease in BIX through time, while BIX in the stream increased (Figure 5d).

The ratio of fluorescence peak C to peak A (C/A) ranged from 0.99 to 2.01 in leaf leachates, and the mean was greater than all other locations (Table 1). C/A ranged from 0.62 to 0.74 in the stream, 0.57 to 0.99 on the south facing aspect and 0.59 to 0.89 on the north facing aspect (Figure 5e). C/A in the stream was significantly lower than all lysimeter locations except 30 cm south facing lysimeters (Table 1). Both the north aspect and stream showed decreasing trends through time in C/A (Figure 5e).

4. Discussion

Our primary objective was to investigate how changes in snowmelt timing affect both the amount and quality of DOM delivered from soils to streams. Through a comparison of snowmelt on north versus south-facing hillslopes within the same watershed, we observed a correlation between runoff and north aspect soil moisture, whereas the south aspects exhibited no correlation with runoff (Figure 3). Furthermore, stream DOM character did not correlate with that of the south-aspect soils (Table 1). The varying trends between aspects demonstrate the different soil wetting regimes through the melt, which over long time periods are also apparent in the increased podzolization in the north aspect soils (Hunckler & Schaetzl, 1997; Schaetzl & Isard, 1996; Schaetzl et al., 2018; Table S1 in Supporting Information S1). We discuss below how these factors regulate the quality of DOM delivered from soils to the stream over the course of snowmelt, and explore how changes in stream DOM composition reflect the source of organic matter and its processing within soils on different aspects (Figure 6).

4.1. How Does Stream DOM Track With Snowmelt?

Contrary to our hypothesis, stream DOC concentrations did not track the snowmelt hydrograph (Figure 4). This contradicts prior work in a montane watershed exhibiting a snowmelt-dominated hydrograph with similar

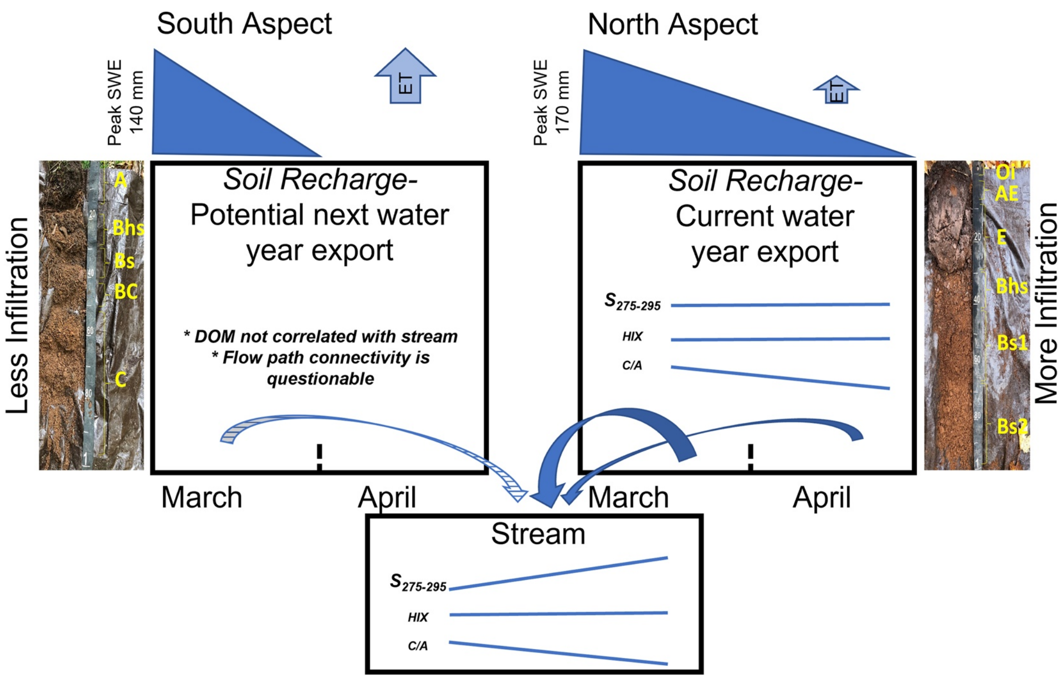

Figure 6. A conceptual model of dissolved organic matter (DOM) export changes with geomorphic aspect. In these soils, nearly all of the organic matter is located in the top 30 cm, with broader organic horizons and more profile development on north facing slopes. South facing slopes in Michigan have less infiltration of peak snow water equivalent (SWE) and therefore have shallower depths to parent material (C horizon) than north facing aspects (Hunckler & Schaetzl, 1997). We suggest that these changes in infiltration result in stream DOM character largely influenced by soil DOM composition on the north facing aspects, particularly with changes in C/A (declining trend over time for soil and stream). Owing to the very high permeability (15–51 cm per hour [USDA Soil Conservation Service, 1991]) and depth (tens of meters) of these sandy soils, we suspect the slow transfer of surface DOM to streams through deeper flow paths on north aspects, with high uncertainty as to deeper flow paths on south aspects.

magnitude of discharge and seasonal DOC concentrations, wherein a tight correlation between stream DOC concentrations and snowmelt flushing was observed (Burns et al., 2016). We attribute the different responses in DOC concentrations with snowmelt to the different soil types in the two studies. In the Burns et al. (2016) study, north aspect soils were Inceptisols (a complex of Dystrocryepts and Haplocryepts) and south aspect soils were also poorly developed and shallow (lithic, <1 m). Additionally, in our study stream discharge did not exhibit a threshold response to soil VWC, as has been reported for mountain catchments (Penna et al., 2011). Rather, we observed a linear relationship on the north-facing aspect and no significant relationship on the south-facing aspect (Figure 3). The Spodosols of our study could attenuate DOC flushing to the stream in surface runoff, with supply occurring from deeper within the soil profile. Moreover, surface litter-derived DOM dominates the character of mineral soil horizon DOM in Spodosols (Rothstein et al., 2018), which offers a parsimonious explanation for the much higher HIX values in our stream (mean HIX = 10.9) compared with those measured in Burns et al. (2016) (minimum HIX = 1.80; maximum HIX = 3.85). While an evaluation of antecedent (before freshet) soil moisture conditions in these studies was outside the scope of this study, these findings demonstrate that streams with similar snowmelt-dominated hydrographs and watershed characteristics can exhibit quite different DOM composition and DOC export dynamics, due to differences in soil properties and associated flow paths.

This study highlights the importance of soil parent material in governing infiltration versus overland flow. For example, in a similar forested watershed in New York underlain with glacially transported till, overland flow was deemed a minor source to the stream constrained to a portion of the rising limb of the hydrograph (Inamdar & Mitchell, 2007). Yet, the New York watershed featured a low-permeability clay layer in the surface soil, which facilitated shallow subsurface flow. The deep glacially transported parent material (moraine till) underlying the watershed described herein distinguishes this study from other watershed studies. There is a rich literature examining deeper flow pathways and runoff generated by the connection between soil water and the soil-bedrock interface during snowmelt (see Bracken & Croke, 2007; McNamara et al., 2005; Xiao et al., 2019), and the importance of DOC flushing from hillslopes along this flow path (McGlynn & McDonnell, 2003; Wen et al., 2020). We suggest that highly permeable and deep sandy Spodosols (glacial moraines), with bedrock tens of meters below the surface, do not permit the tight coupling between runoff and peak flushing observed in other studies (Boyer et al., 1997, 2000; Perdrial et al., 2018, 2014). Rather, there appears to be a "slow drip" of DOM continuously supplied to the stream, and in particular from the north facing aspect (Figure 6). This could explain in part why DOC concentrations did not track the hydrograph peak, and remained unchanged even as the stream approached baseflow conditions (Figure 4). We have observed seeps flowing out of the mineral soil near the stream bank (Figure S4 in Supporting Information S1), which would represent contributions from deeper flow paths. Composition measurements of two seep samples taken in mid-March were more similar to the stream and north-aspect soils than the south aspect soils (mean (±SE): HIX, BIX, and C/A of 10.7 ± 1.3, 0.55 ± 0.01 and 0.69 ± 0.02, respectively; confer with Table 1). Such seep contributions of DOM were also significant in the till-soil watershed described by Inamdar and Mitchell (2007). Taken together, we suggest that the effects of snowmelt in watersheds underlain with glacial-till parent materials on stream recharge and DOM character differ from other soil types, particularly during peak runoff and baseflow conditions (Barnhart et al., 2016; Carroll et al., 2019; Godsey et al., 2014). Further, we suggest that the character of stream DOM over time reflects the slow, steady supply of DOM as it moves through soils that exhibit hydrologic connectedness to the stream, such as those on north-facing aspects (Figure 6).

DOM characterized by several of the absorbance and fluorescence indices indicated a consistent degree of processing for the DOM delivered to the stream through snowmelt. Interestingly, metrics concretely associated with DOM degradation ($S_{275-295}$, C/A, BIX; (Helms et al., 2013, 2008)) displayed gradual trends toward increased degradation through time in the stream. This result can be expected, as litterfall is a key source of DOM which would be degraded over time. The decline in C/A over time suggests a change in the DOM pool to one which is more degraded or oxidized, which is consistent with prior work showing the decline in C/A in long-term incubations of lake water (Kothawala et al., 2012), as well as with the photodegradation of soil and plant leachates (Hansen et al., 2016). With measurements taken in the fall season, one would expect C/A to cycle back to higher levels.

In addition to tracking trends in DOM degradation over time, changes in DOM composition were likely tracking exports primarily from the north-facing aspect. For example, declining trends in $S_{275-295}$, C/A and BIX could have been reflecting decreasing hydrologic connection between south aspects and stream as the south aspect gradually dried out. We suggest that the decreased infiltration on the south aspect, owing to decreased peak SWE and increased evaporation and drier soils at the onset of the melt, decreased or uncoupled the connectivity of this landscape position from the stream (Figure 6). On the other hand, BIX and C/A measured in the stream tracked BIX and C/A in the north aspect soils throughout the study. These trends are consistent with asynchronous snowmelt occurring on different landscape positions, and therefore gradual shifts in the timing of DOM contributions from different sources to the stream through snowmelt (cf. Boyer et al., 2000). However, different optical properties of DOM varied in their ability to differentiate DOM sources from leaf leachates and soils as they were transported to the stream with the progression of snowmelt.

4.2. How Does DOC Vary Optically Among Leaf Leachates, Soil Water and Stream?

The spectral slope metrics $S_{275-295}$ and $S_{350-400}$ differed from one another in this study. Specifically, $S_{275-295}$ appeared significantly different among soil locations and stream while also displaying a seasonal trend in the stream (Table 1; Figure 5). Simultaneously, $S_{350-400}$ displayed neither of these characteristics. Previous research has identified $S_{275-295}$ as a more sensitive metric to DOM degradation (Helms et al., 2013, 2008), however, these studies have reported overall largely similar trends between the two metrics. In our study, $SUVA_{254}$ was similar between leaf leachates, north facing B horizon, and the stream, while $S_{275-295}$ displayed significant differences among these sample locations. The general pattern of low $SUVA_{254}$ corresponding to high $S_{275-295}$ (Helms et al., 2008) was also observed in this study, suggesting $S_{275-295}$ may be tracking some pool of relatively low-aromaticity or freshly sourced DOM (and in this case, DOM extracted with DI H_2O). Our results suggest that $S_{275-295}$ is more responsive to DOM alteration in the terrestrial-aquatic interface whereas $S_{350-400}$ represents a broader pool of more ubiquitous DOM (Table 1).

HIX was the only fluorescence metric which differentiated A horizon (15 cm soil depth) DOM between aspects (Table 1), suggesting that HIX is most sensitive to differences in DOM processing within the upper 15 cm of soil

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out of the metrics we examined. South-facing 30 cm lysimeters (B horizon) were not differentiated from A horizon soils in any metric, yet B horizons in north-facing soils displayed significantly different $SUVA_{254}$, $S_{275-295}$, HIX, and BIX from A horizon lysimeters. We suggest B horizon DOM represents a fraction of more processed DOM as a result of its residence time in the A horizon and preferential removal of aromatic lignin derivatives through metal complexing in these soils (Kaiser & Guggenberger, 2000). In support of this, soil HIX increased on both aspects through the snowmelt period, further deviating from leaf litter HIX values (Figure 5). Because HIX values diverged from litter sources, we suggest within soil processing of fresh inputs was likely responsible for these high HIX values. We expected BIX to be a better indicator of "fresh" inputs like the leaf leachates, but these data suggest BIX is perhaps not well suited for tracking diagenesis of DOM in soils (see also, Meingast, Grunert, et al., 2020).

C/A was the only metric to show a consistently declining trend from leaf leachates, to A and B horizons, and finally to the stream. Both C and A peaks are within the humic-like region of fluorescence, and the peaks are likely tracking a similar fraction of DOM (Coble, 1996; Hansen et al., 2016). Given this, we postulate that C/A (particularly peak C) was tracking a consistent humic-like DOM fraction of compounds through our study which was: (a) not easily adsorbed by soils or biologically removed, (b) not strongly influenced by processes altering HIX, BIX or spectral slopes, and (c) representing a fraction whose fluorescence was able to directly or indirectly be altered within soils. Given these factors, we suggest that C/A in our study was tracking partial oxidation of lignin-like derivatives from the humic-like DOM pool which was sourced from inputs such as leaf litter and yet not easily complexed by soils.

Previous research using long-term incubations of lake water under dark conditions showed the selective removal of peak C relative to peak A, thus suggesting biodegradation and not photooxidation (Kothawala et al., 2012). If C/A were tracking a selective removal of a different DOM fraction, likely hydrophobic acids in Spodosols (Dai et al., 1996), we would expect the B horizons of the more developed north aspect soils to display the lowest values of C/A. However, B horizons on the south aspect displayed the lowest C/A values. Our study suggests that C/A may be the most applicable metric for tracking the diagenesis of the translocated DOM. We hypothesize C/A is likely tracking hydrophilic acid and/or hydrophilic neutral fractions (Qualls & Haines, 1991), which is consistent with the study by Kothawala et al. (2012), who found inconsistent changes in incubated DOM character using other spectral indices. Indices such as $SUVA_{254}$, $S_{275-295}$, HIX, and BIX are likely altered by removal of DOM fractions but it is not clear if these indices reflect changes in specific pools of DOM or rather are tracking changes in bulk DOM. Further work examining the extent to which these indices track alteration of specific sources of DOM—and particularly organo-mineral complexation (Lei et al., 2020)—as opposed to selective loss of fluorophores is needed to extend the application of these indices as tracers of DOM in the terrestrial-aquatic interface in these soil types.

The varying patterns over time through soil profiles and into the stream illustrate some of the difficulties of using optical metrics to infer source of DOM (cf. Burns et al., 2016). Overall, this study highlights the utility of fluorescence and absorption spectroscopy in understanding within-season changes in DOM properties at the terrestrial-aquatic interface. We found fluorescence metrics, specifically C/A, to add additional insights into DOM diagenesis through soils and into streams which were not evident in absorption measurements. Future work combining mass spectroscopy in probing the response of these DOM fractions to borohydride reduction of ketone and aldehyde functional groups (Andrew et al., 2013; Osburn et al., 2019) could further distinguish the source of B horizon DOM, and its diagenesis, by tracking partial oxidation of ketones and aldehydes to carboxylic acids.

4.3. What Are the Implications for DOM Composition Under a Changing Climate?

The climate of northern regions is anticipated to change in ways that lead to an earlier and more prolonged snowmelt period in the spring (Ashley et al., 2020; Musselman et al., 2017). Even though rain-on-snow events are likely to increase in lake-effect snow dominated areas as winters become warmer (Crossman et al., 2016), it is unlikely that winter snowpack will decrease enough to remove hydrologic connectivity in soils and streams during snowmelt (Meingast, Kane, et al., 2020; cf. Casson et al., 2012). Earlier snowmelt during periods with lower sun angles and less incident solar radiation would increase wetting pulses in soils (e.g., north aspect; Figure 3c; Musselman et al., 2017; Schaetzl & Isard, 1996). As such— and perhaps counterintuitively—the north aspects described in this study could be more representative of these earlier and slower melt patterns. These factors are likely to increase the vertical movement of DOM (spodic soil horizon development), increasing the amount of humic material stabilized in the soil, as well as increasing the fraction of less humic-like (lower HIX) and lower molecular weight (higher $S_{275–295}$) character of DOM reaching the stream (Figure 6). A recent synthesis of north temperate lakes has shown that years with earlier snow melt and earlier spring runoff result in less phytoplankton production (lower chlorophyll-*a*; Hrycik et al., 2021). Such changes in DOM character described in this study could transmit across the landscape, altering DOM delivered to downstream aquatic ecosystems with consequences for light penetration, macro and micro-nutrient availability, and biological productivity. Here, we have shown that changes in snowmelt dynamics associated with climate change have the ability to significantly alter the pool of DOM mobilized from soils and into streams. We suggest that soil type should be considered in broad assessments of DOM export responses to the changes in snowmelt expected to occur in a warmer climate.

Data Availability Statement

The raw data for the findings described herein are available in the public domain through PANGAEA (https://doi.pangaea.de/10.1594/PANGAEA.922588).

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