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Dissolved Organic Carbon Turnover in Permafrost-Influenced Watersheds of Interior Alaska: Molecular Insights and the Priming Effect

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Increased permafrost thaw due to climate change in northern high-latitudes has prompted concern over impacts on soil and stream biogeochemistry that affect the fate of dissolved organic carbon (DOC). Few studies to-date have examined the link between molecular composition and biolability of dissolved organic matter (DOM) mobilized from different soil horizons despite its importance in understanding carbon turnover in aquatic systems. Additionally, the effect of mixed DOM sources on microbial metabolism (e.g., priming) is not well understood. No studies to-date have addressed potential priming effects in northern high-latitude or permafrost-influenced aquatic ecosystems, yet these ecosystems may be hot spots of priming where biolabile, ancient permafrost DOC mixes with relatively stable, modern stream DOC. To assess biodegradability and priming of DOC in permafrost-influenced streams, we conducted 28 day bioincubation experiments utilizing a suite of stream samples and leachates of fresh vegetation and different soil horizons, including permafrost, from Interior Alaska. The molecular composition of unamended DOM samples at initial and final time points was determined by ultrahigh resolution mass spectrometry. Initial molecular composition was correlated to DOC biodegradability, particularly the contribution of energy-rich aliphatic compounds, and stream microbial communities utilized 50–56% of aliphatics in permafrost-derived DOM within 28 days. Biodegradability of DOC followed a continuum from relatively stable stream DOC to relatively biolabile DOC derived from permafrost, active layer organic soil, and vegetation leachates. Microbial utilization of DOC was ∼3–11% for stream bioincubations and ranged from 9% (active layer mineral soil-derived) to 66% (vegetation-derived) for leachate bioincubations. To investigate the presence or absence of a priming effect, bioincubation experiments included treatments amended with 1% relative carbon concentrations of simple, biolabile organic carbon substrates (i.e., primers). The amount of DOC consumed in primed treatments was not significantly different from the control in any of the bioincubation experiments after 28 days, making it apparent that the addition of biolabile permafrost-derived DOC to aquatic ecosystems will likely not enhance the biodegradation of relatively modern, stable DOC sources. Thus, future projections of carbon turnover in northern high-latitude region streams may not have to account for a priming effect.

KEY POINTS

- Biodegradability of DOC followed a continuum from relatively stable stream DOC to relatively biolabile DOC from permafrost, active layer organic soil, and vegetation leachates.
- DOM composition, especially the relative contribution of aliphatic compounds, largely controlled biodegradability and we observed evidence for selective utilization/preservation of certain compounds with depth in soil horizons.
- Nutrient availability played a role in DOC biodegradability, while priming did not appear to be a relevant mechanism for enhancing DOC biodegradation.

Keywords: dissolved organic matter, dissolved organic carbon, biodegradation, permafrost, leachates, priming

INTRODUCTION

Climate change in northern high-latitudes (Acia, 2005; Settele et al., 2014) has prompted concern over changes in soil and stream biogeochemistry that affect the fate of dissolved organic carbon (DOC). Increasing permafrost thaw associated with warming in these regions is of particular concern as permafrost soils currently store approximately twice as much carbon as in the Earth's atmosphere (Zimov et al., 2006; Schuur et al., 2008; Tarnocai et al., 2009). As near-surface permafrost thaws and maximum thaw depth in the summer increases (Zhang, 2013), more permafrost-derived DOC will be mobilized (Wickland et al., 2018) and exported to streams, where it has been shown to be highly susceptible to microbial degradation (Mann et al., 2014; Spencer et al., 2015; Vonk et al., 2015; Drake et al., 2017; Stubbins et al., 2017). Therefore, permafrost thaw represents a potential positive feedback to the atmosphere as aged permafrost carbon may enter the contemporary carbon cycle as DOC is mobilized (Schuur et al., 2008; Schaefer et al., 2011; Spencer et al., 2015) and remineralized as CO_2 in the aquatic pathway due to microbial respiration.

Warming may also affect the molecular composition of dissolved organic matter (DOM) exported to streams in discontinuous permafrost regions, which is inherently linked to the biodegradability of DOC (Dittmar and Kattner, 2003; Mann et al., 2012; Ward and Cory, 2015; O'Donnell et al., 2016). Microbial turnover of DOC previously stored in frozen soils is critical to our knowledge of how carbon export in high-latitude streams will respond to climate change (Striegl et al., 2005; Zhang et al., 2017). However, limited studies have examined the link between molecular composition and biolability of DOM mobilized from different soil horizons despite its importance in understanding carbon turnover in aquatic systems. While biodegradability of DOC is an overriding control on ecosystem respiration, regulating how much organic carbon (OC) is remineralized as CO_2 or exported downstream (Holmes et al., 2008, 2012; Mann et al., 2012; Wickland et al., 2012; Abbott et al., 2014), the processes controlling DOC degradation are not well understood (Mann et al., 2012; Wickland et al., 2012; Vonk et al., 2015), particularly the effect of mixed DOM sources on microbial metabolism (e.g., priming).

Boreal and arctic discontinuous permafrost regions are hot spots for DOC degradation, especially at the soil-stream interface (Hutchins et al., 2017). This provides an opportunity to study microbial responses to the presence of mixed DOC sources, which can lead to increased respiration compared to the sum of the sources alone (Attermeyer et al., 2014). Soil studies have demonstrated enhanced carbon turnover due to a "priming effect" (Bingeman et al., 1953) in which moderate inputs of biolabile substrates enhance microbial degradation and mineralization of more stable OC (Bingeman et al., 1953; Kuzyakov, 2010; Guenet et al., 2012). Priming is well documented in the soil sciences, however, it has only recently been suggested in the aquatic sciences, and studies in a variety of aquatic ecosystems have yielded both evidence for and against a priming effect (Guenet et al., 2010, 2014; Bianchi, 2011; Bengtsson et al., 2014, 2018; Hotchkiss et al., 2014; Koch et al., 2014; Bianchi et al., 2015; Catalán et al., 2015; Ward et al., 2017; Textor et al., 2018).

No studies to-date have addressed priming effects in northern high-latitude, permafrost-influenced aquatic ecosystems, yet they may be hot spots of priming as highly biolabile permafrost DOC mixes with modern, stable stream DOC (Abbott et al., 2014). Additionally, hot moments of priming have the potential to enhance microbial respiration in northern high-latitude streams and rivers; during spring freshet, a large proportion of biolabile DOC is exported in a short time period (Striegl et al., 2005; Raymond et al., 2007; Spencer et al., 2008, 2009; Holmes et al., 2012; Wickland et al., 2012) and in summer and fall, DOC from newly thawed permafrost soils may be released (Drake et al., 2015; Wickland et al., 2018). As riverine processing of allochthonous DOC is a critical component of the global carbon cycle, the importance of priming is underscored by its potential as a missing link in the study of mechanisms that may be contributing to removal of terrigenous DOM from the ocean (Bianchi, 2011).

This study was conducted to investigate: (1) how the molecular composition of DOM leached from various terrestrial sources affects DOC bioavailability in streams; and (2) if the mixing of fresh inputs of terrestrial DOM, specifically permafrost DOC, can "prime" relatively modern, stable stream DOC in northern high-latitudes, resulting in enhanced DOC respiration. Samples were collected in the Yukon River Basin in interior Alaska, a region underlain by discontinuous permafrost that has recently been subject to rapidly warming temperatures (Osterkamp, 2007; Chapin et al., 2010; IPCC, 2013), permafrost thaw and degradation (Osterkamp, 2007; Lu and Zhuang, 2011; Belshe et al., 2013) and associated changes in hydrology and vegetation (Neff and Hooper, 2002; Schuur et al., 2007; Wickland et al., 2007; Walvoord et al., 2012; Jorgenson et al., 2013). We quantified the biodegradability of DOC in streams as well as vegetation and soil leachates during 28 day bioincubation experiments. The molecular composition of the various DOM sources at initial and final timepoints was determined via ultrahigh resolution mass spectrometry to investigate which DOM compound classes are particularly susceptible to microbial utilization. The role of priming was determined by statistical differences between DOC turnover in controls and bioincubation treatments amended with a variety of biolabile OC substrates such as acetate, a low molecular weight acid that is highly bioavailable and abundant in ancient permafrost DOM (Drake et al., 2015). By assessing possible controls on DOC biodegradability in a variety of sources, we can address the urgent need to understand the fate of allochthonous DOM released into streams by thawing and leaching processes and the mechanisms controlling DOC turnover in permafrost landscapes.

MATERIALS AND METHODS

Site Descriptions and Sample Collection

Sampling occurred at four different watersheds underlain by discontinuous permafrost in the Yukon River Basin of Interior Alaska (**Figure 1**). Seasonal discharge patterns in the region are commonly used to divide seasons into spring flush (May through June), summer to fall (July through October), and winter (November through April) (Striegl et al., 2005). Stream samples were collected at all four sites during spring flush and at two of the sites during the fall (**Table 1**). Old Man Stream is an afforested, silty lowland site while the remaining sites are uplands forested with black spruce (*Picea mariana*) (**Table 1**). Richardson Tributary and Erickson Thermokarst (TK) watersheds are classified as silty, while West Fork Dall Creek watershed is classified as rocky (**Table 1**; Jorgenson et al., 2013). On each sampling occasion, a 4 L bulk stream sample was filtered through a pre-rinsed high capacity 0.45 μm capsule filter and the filtrate was collected in an acid-washed, high-density polyethylene (HDPE) bottle. In addition 1 L of stream water was filtered through a GF/A (1.6 μm) glass microfiber filter (precombusted at 450°C, >5 h) and collected in acid-washed, polycarbonate bottles for use as an inoculum in bioincubations (see below). Samples were stored in the dark at 4°C until bioincubations were setup.

Groundcover vegetation and soil samples from the active layer and near-surface permafrost were collected during spring sampling at the two sites where seasonal stream sampling occurred at an active thermokarst slump (Erickson TK watershed), and a lowland underlain by discontinuous permafrost (Old Man watershed). Representative groundcover vegetation, mostly feather mosses and vascular plants, was collected with a soil knife directly above the location of soil collection. At the Old Man site, a SIPRE (Snow, Ice, and Permafrost Research Establishment) corer (7.5 cm diameter, 1 m length) was used to collect soils after the groundcover vegetation was removed. Three replicate cores that included seasonally frozen active layer soils and near-surface permafrost soils were taken within the same area (~25 m^2), which had an approximate active layer depth of ~40–65 cm based on measurements at the same site the previous fall. Cores were extruded, wrapped in aluminum foil at the field site, and kept frozen on dry ice during transport to laboratory facilities. The site at Erickson TK is an active incised thermokarst slump where samples were collected at multiple depths along the face of the exposed soil profile using a soil knife and hand trowel. Exposed soil layers were first removed from the face of the slump and underlying, unexposed soils were collected. Vegetation and soil samples were stored in the dark on dry ice immediately following sample collection.

Vegetation and Soil Leachates

Leachates were made from the groundcover vegetation and soil samples collected from Erickson TK and Old Man watersheds. Soils were classified as organic (active layer), mineral (active layer), or permafrost based on depth of horizon (**Table 2**). Soils collected at three discrete depths from Erickson TK were leached individually. The frozen soil cores from Old Man were cut into discrete depth increments using a band saw. Replicate corresponding soil layers (organic active layer, mineral active layer, and permafrost) from the three cores were combined prior to leaching. Materials were leached in a 0.001 N sodium bicarbonate ($NaHCO_3$) solution of ultrapure water, as $NaHCO_3$ acts as a pH buffer that simulates the ionic strength of the sampled systems (Wickland et al., 2007; Spencer et al., 2008). Dried vegetation (50°C for 24 h) was added to the buffer solution in a 1:4 ratio by weight, while field-moist frozen soils were homogenized with a mallet and added in a 1:2 ratio by weight. Vegetation and soils were leached at room temperature (20°C) in the dark on a stir plate for 24 h before filtering. Leachates were filtered through high capacity capsule filters (0.45 μm) using a peristaltic pump (Cole and Parmer, Masterflex L/S) and immediately used for bioincubation experiments.

Bioincubation Experiments

Filtered (0.45 μm) stream samples and leachates were amended with a 1% microbial inoculum (Wickland et al., 2012; Vonk et al., 2015) obtained from stream samples from each site filtered with precombusted (450°C, 5 h) GF/A (1.6 μm) glass microfiber filters. An unamended control treatment quantified background DOC loss, while all other treatments were nutrient-amended to observe DOC loss under nutrient replete conditions. Nutrients were added for each sample based on doubled Redfield ratios

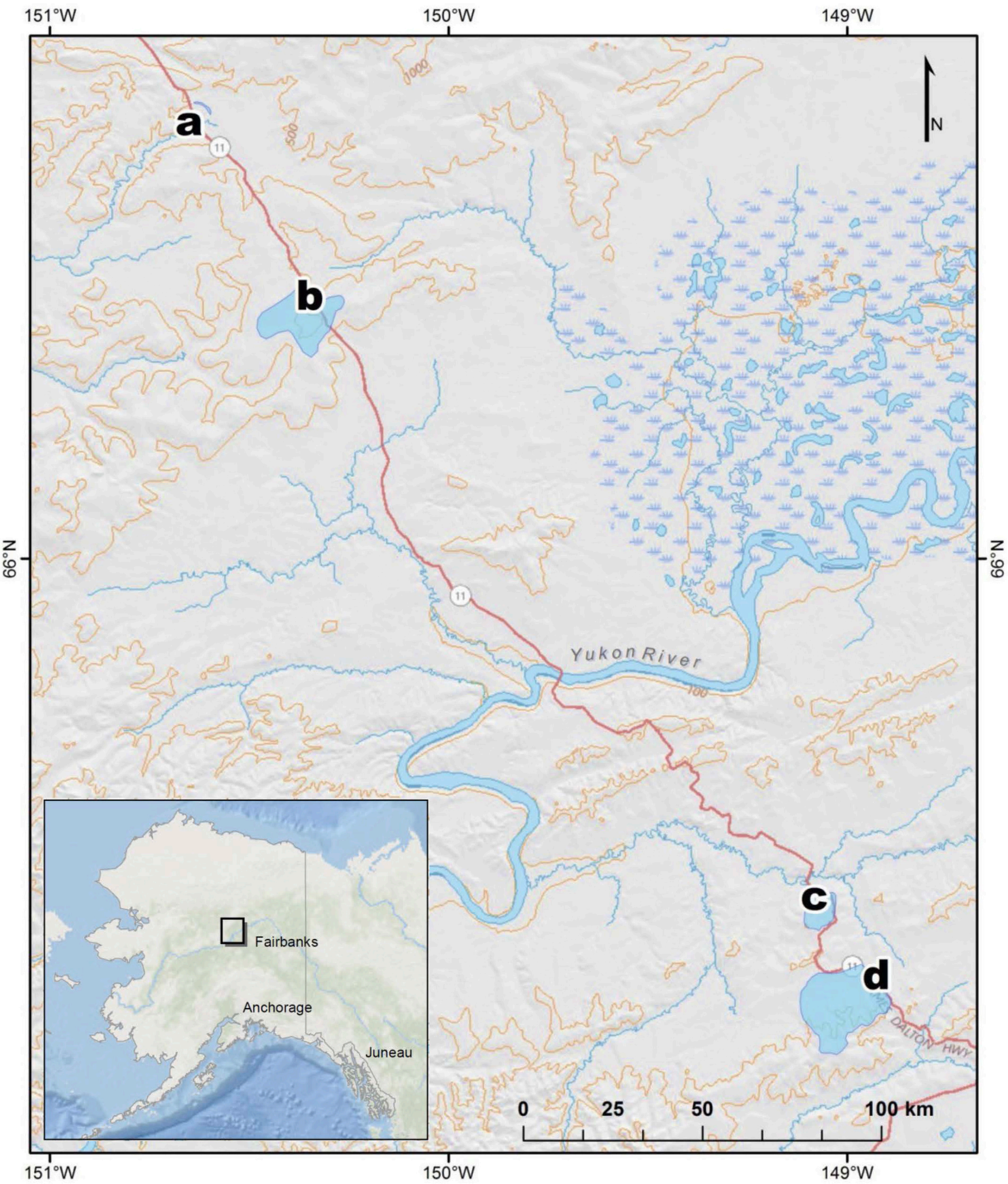

FIGURE 1 | Map of stream sampling site locations and watersheds in Interior Alaska, United States, at **(a)** Old Man, **(b)** West Fork Dall, **(c)** Richardson, and **(d)** Erickson TK.

of inorganic nitrate and phosphate in the form of KNO_3 and Na_3PO_4 (i.e., 106C: 32N: 2P; Mann et al., 2015; Vonk et al., 2015). Therefore, an equal proportion of nutrients was added to each sample, accounting for differences in initial DOC concentrations between samples. To test for a priming effect with carbon as the limiting factor, there were three separate treatments of biolabile OC substrates (e.g., primers) plus the same proportion of KNO_3 and Na_3PO_4. Primer treatment groups were amended with 1% relative carbon concentrations of acetate ($C_2H_9NaO_5$), glucose ($C_6H_{12}O_6$), or cellobiose ($C_{12}H_{22}O_{11}$) based on the initial concentration of filtered, unamended samples. The 1% primer amendment was chosen based on the upper range of previously tested primer amendments (Catalán et al., 2015). Stream bioincubation experiments consisted of a five-point time

TABLE 1 | Site information for stream sampling in the Yukon Flats, Interior Alaska.

Site	Description	Soil type	Coordinates		Collection date	Season
Richardson Tributary	forested (*P. mariana*) upland	Silty	65.64986	−149.08145	05-17-17	S
West Fork Dall Creek	forested (*P. mariana*) upland	Rocky	66.26826	−150.34721	06-16-17	S
Erickson TK Stream	forested (*P. mariana*) upland	Silty	65.57191	−148.92633	05-15-17	S
					09-12-17	F
Old Man Stream	afforested lowland	Silty	66.44698	−150.62128	05-16-17	S
					09-12-17	F

TABLE 2 | DOC concentration, ΔDOC over 28 days, and percent of biodegradable dissolved organic carbon (BDOC), all reflecting the average and standard deviation of triplicate samples.

Site	DOC (mg L^{-1})	ΔDOC (mg L^{-1})	% BDOC
Streams (Spring)			
Richardson Trib	39.9 ± 0.3	1.7 ± 0.3	4.2 ± 0.7
West Fork Dall	18.5 ± 0.5	2.1 ± 0.3	11.1 ± 1.4
Erickson TK	30.0 ± 0.9	1.1 ± 0.3	3.7 ± 1.0
Old Man	14.0 ± 0.2	1.0 ± 0.1	7.0 ± 0.9
Streams (Fall)			
Erickson TK	30.4 ± 0.1	0.7 ± 0.3	2.4 ± 0.9
Old Man	20.6 ± 0.3	0.3 ± 0.6	1.7 ± 3.1
Leachates (Spring)			
Erickson TK			
Vegetation (0–10 cm)	69.1 ± 0.4	42.8 ± 0.5	62.0 ± 0.7
Organic Soil (11–24 cm)	27.7 ± 0.6	11.9 ± 0.2	42.9 ± 0.8
Mineral Soil (25–38 cm)	9.7 ± 0.1	2.8 ± 0.5	29.0 ± 4.6
Permafrost (180–197 cm)	19.0 ± 0.6	6.5 ± 0.2	34.3 ± 1.0
Old Man			
Vegetation (0–13 cm)	140.6 ± 0.9	93.0 ± 0.2	66.2 ± 0.1
Organic Soil (14–31 cm)	63.0 ± 0.3	28.2 ± 0.4	44.8 ± 0.7
Mineral Soil (41–61 cm)	25.8 ± 0.1	2.3 ± 0.1	9.0 ± 0.5
Permafrost (70–90 cm)	34.6 ± 0.1	3.9 ± 0.2	11.4 ± 0.7

DOC concentration was obtained from initial control samples. ΔDOC was calculated by subtracting the final DOC concentration from the initial DOC concentration. Biodegradable dissolved organic carbon (BDOC) values reflect the proportion of DOC consumed in 28 days. "TK" = thermokarst.

series (0, 2, 7, 14, and 28 days), while leachate bioincubations only had two time points (0 and 28 days) to assess DOC loss.

Triplicate 30 mL samples from each treatment and time point were partitioned into 40-mL acid-washed, precombusted (550°C, 5 h) amber glass vials capped with plastic lids sealed by Teflon-coated septa. Bioincubations were conducted in the dark at room temperature (20°C). At each time point, samples were filtered with 0.45 μm glass microfiber syringe filters to remove any microbial biomass (Vonk et al., 2015) and acidified to pH 2 using 12 M HCl and stored in the dark at 4°C until analysis. Every 7 days remaining samples in the time series were opened and aerated to keep the samples oxygenated.

Dissolved Organic Carbon Analyses

Dissolved organic carbon concentrations of the bioincubation sample sets were analyzed on a Shimadzu TOC-L CPH total organic carbon analyzer using the high temperature combustion catalytic oxidation method. All sample sets were tested against a calibration curve consisting of five different standard concentrations from zero to 50 mg L^{-1}. DOC concentration was measured as non-purgeable organic carbon (NPOC), with a maximum coefficient of variance of 2%.

DOC loss was calculated as the difference between the final (t = 28) and average initial (t = 0) concentrations (ΔDOC) for each sample type (i.e., each site and treatment).

$$\Delta DOC = (InitialDOC_{\text{average}} -- FinalDOC_{\text{replicate}}) \quad (1)$$

Biodegradable dissolved organic carbon (BDOC) was calculated as the proportion of DOC loss,

$$BDOC = (\Delta DOC/DOC_{\text{initial}}) \times 100 \quad (2)$$

during the 28 day bioincubation experiments (Vonk et al., 2015).

Molecular-Level Characterization of Dissolved Organic Matter

Concentrations of DOC in initial bioincubation samples were used to calculate the required aliquot volume for solid phase extraction (100 mg Bond Elut PPL, Agilent Technologies) following the method described by Dittmar et al. (2008). We aimed for a target concentration of 40 μg C mL^{-1} for DOM extracts eluted with 1 mL of methanol. Extracts were stored at −20°C before analysis. A 21 tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS; National High Magnetic Field Laboratory, Tallahassee, FL, United States) was used to analyze the molecular composition of DOM extracts of initial and final control bioincubation samples for each site. The instrument was set to negative ion mode and produced ions via electrospray ionization (ESI). Due to its high resolving power and extreme mass accuracy, ESI-FT-ICR MS is currently unparalleled in its ability to characterize DOM as it can detect thousands of individual molecular peaks separated out in a spectrum by their mass to charge ratio (m/z) (Sleighter and Hatcher, 2007; D'Andrilli et al., 2015; Hendrickson et al., 2015; Smith et al., 2018).

Molecular formulae obtained from FT-ICR MS analysis were assessed in the mass range of 170–1500 m/z and reassigned in PetroOrg Software (Corilo, 2015). Here, we included elemental combinations of C_{1-45} $H_{1-92}N_{0-4}O_{1-25}S_{0-2}$ with mass errors less than 300 ppb and excluding noise signals (>6 σ root mean square baseline noise) (O'Donnell et al., 2016). Elemental stoichiometries and modified aromaticity indices (AI_{mod}; Koch and Dittmar, 2006, 2016) were used to assign molecular formulae into seven different compound classes as follows using a script developed by Hemingway (2017): unsaturated phenolic low O/C = $AI_{mod} < 0.5$, $H/C < 1.5$, $O/C < 0.5$, unsaturated phenolic high O/C = $AI_{mod} < 0.5$, $H/C < 1.5$, $O/C \geq 0.5$, polyphenolic = AI_{mod} 0.50–0.67, condensed aromatic = $AI_{mod} > 0.67$, aliphatic = $H/C \geq 1.5$, $O/C < 0.9$, $N = 0$, sugar-like = $O/C > 0.9$, and peptide-like = $H/C \geq 1.5$, $O/C < 0.9$ $N \geq 1$ (O'Donnell et al., 2016). Although molecular peaks detected during FT-ICR MS may represent multiple isomers, we interpret DOM composition based on the relative abundance of molecular formulae assigned to each compound class. Thus molecular formulae assigned to the same compound class may herein be collectively described as compounds. In this study, shifts in DOM composition due to changes in relative abundance of different compound classes are attributed to selective microbial utilization of certain compounds.

Statistical Analyses

Student's *t* tests were performed to assess the presence or absence of nutrient and priming effects in the bioincubation experiments. To test for a priming effect, the amount of DOC consumed over 28 days (ΔDOC mg L^{-1}) in the nutrient-amended control was compared to each nutrient-amended primer treatment group. A significant difference ($p < 0.05$) in DOC consumption would indicate that a priming effect occurred. Nutrient effects were indicated by a significant difference in DOC consumption between the unamended control and nutrient-amended control.

Additionally, we used Spearman rank correlations to assess the relationship between biodegradability and chemical composition of stream and leachate DOM. Spearman correlations were performed between percent BDOC and relative abundance of common compounds (present in $\geq$50% of samples) obtained from FT-ICR MS analysis. Only compounds that were significantly correlated ($p < 0.05$) with BDOC were assigned a Spearman rank coefficient and plotted in van Krevelen space (O:C vs. H:C).

RESULTS

Biodegradability of Stream and Leachate Dissolved Organic Carbon

Initial background DOC concentrations of stream samples collected in spring ranged from 14.0 to 39.9 mg L^{-1} (**Tables 1**, **2**). On average, 1.5 ± 0.5 mg L^{-1} DOC was lost over 28 days and the proportion of BDOC was 6.5 ± 3.2% (**Figure 2** and **Table 2**). For comparison, our stream BDOC values fall on the lower range of those reported by Kawahigashi et al. (2004), who found 4–28% BDOC in permafrost-influenced streams, but this also included continuous permafrost regions which tend to have higher BDOC values (Vonk et al., 2015). Samples collected in the fall had background DOC concentrations that were 1.6 and 47.1% higher compared to spring at Erickson TK Stream and Old Man Stream, respectively (**Table 2**). In contrast, the proportions of BDOC at these sites were slightly lower in fall, averaging 2.0 ± 0.5% compared to 5.4 ± 2.4% in spring (**Table 2**).

Leachates of vegetation and active layer organic soils collected at the Old Man site had higher DOC concentrations compared to those at the Erickson TK site (**Table 2**). Leachate DOC exhibited a distinct pattern of biodegradability that was consistent across sites. Vegetation DOC was the most biodegradable, followed by active layer organic soil and permafrost soil DOC, with active layer mineral soil DOC being most stable (**Table 2** and **Figure 3**). Average leachate BDOC was 64.1% for vegetation, 43.8% for active layer organic soil, 19.0% for active layer mineral soil, and 22.8% for permafrost soil across the sites (**Table 2**). Although BDOC values for vegetation and active layer organic soil leachates were comparable at the two sites, active layer mineral soil and permafrost soil leachates had much higher BDOC values at the Erickson TK site than the Old Man site (**Table 2**).

Molecular Composition of Stream and Leachate Dissolved Organic Matter

Dissolved organic matter composition in streams, vegetation, and soil leachates was dominated by unsaturated phenolic compounds, mostly in the high O/C range, as measured by FT-ICR MS (**Table 3** and **Figures 4**, **5**). Although the unsaturated phenolic compound class was most prevalent in all DOM samples, these compounds come from diverse sources, and showed limited changes in relative abundance over the bioincubation period (**Figures 4**, **5**). The next most abundant compound class was polyphenolics followed by condensed aromatics and aliphatics, respectively, while sugar- and peptide-like compounds contributed minimally to the DOM pools (**Table 3** and **Figures 4**, **5**).

Vegetation DOM leachates had the largest relative abundance of aliphatic, sugar-, and peptide-like compounds (**Table 3** and **Figure 5**). The vegetation consisted of vascular plants and mosses, which have been shown to release highly biolabile DOM upon leaching (Wickland et al., 2007; Spencer et al., 2008). Out of all leachate DOM types, vegetation had the smallest contribution of polyphenolic compounds and condensed aromatics (**Table 3** and **Figure 5**), consistent with other studies looking at the chemical composition of these types of mosses (Wickland et al., 2007; Spencer et al., 2008). DOM in the active layer organic soil and permafrost soil leachates had smaller relative abundances of aliphatic and sugar-like compounds in comparison to the vegetation leachates, while there was an increasing contribution of condensed aromatic and polyphenolic compounds in these soil horizons (**Table 3** and **Figure 5**). However, compared to active layer mineral soils, DOM released from permafrost soil appears relatively enriched in aliphatic compounds that are highly susceptible to biodegradation (Vonk and Gustafsson, 2013; Mann et al., 2015; Spencer et al., 2015). The DOM leached from active layer mineral soils in this study had the smallest relative contribution of aliphatic compounds out of any of the leachate DOM samples, and the highest relative abundance of condensed aromatics and polyphenolics overall, including stream DOM samples (**Table 3** and **Figures 4**, **5**).

While stream DOM composition was relatively stable with respect to microbial degradation (**Figure 4**) there was an evident shift in leachate DOM composition by the end of

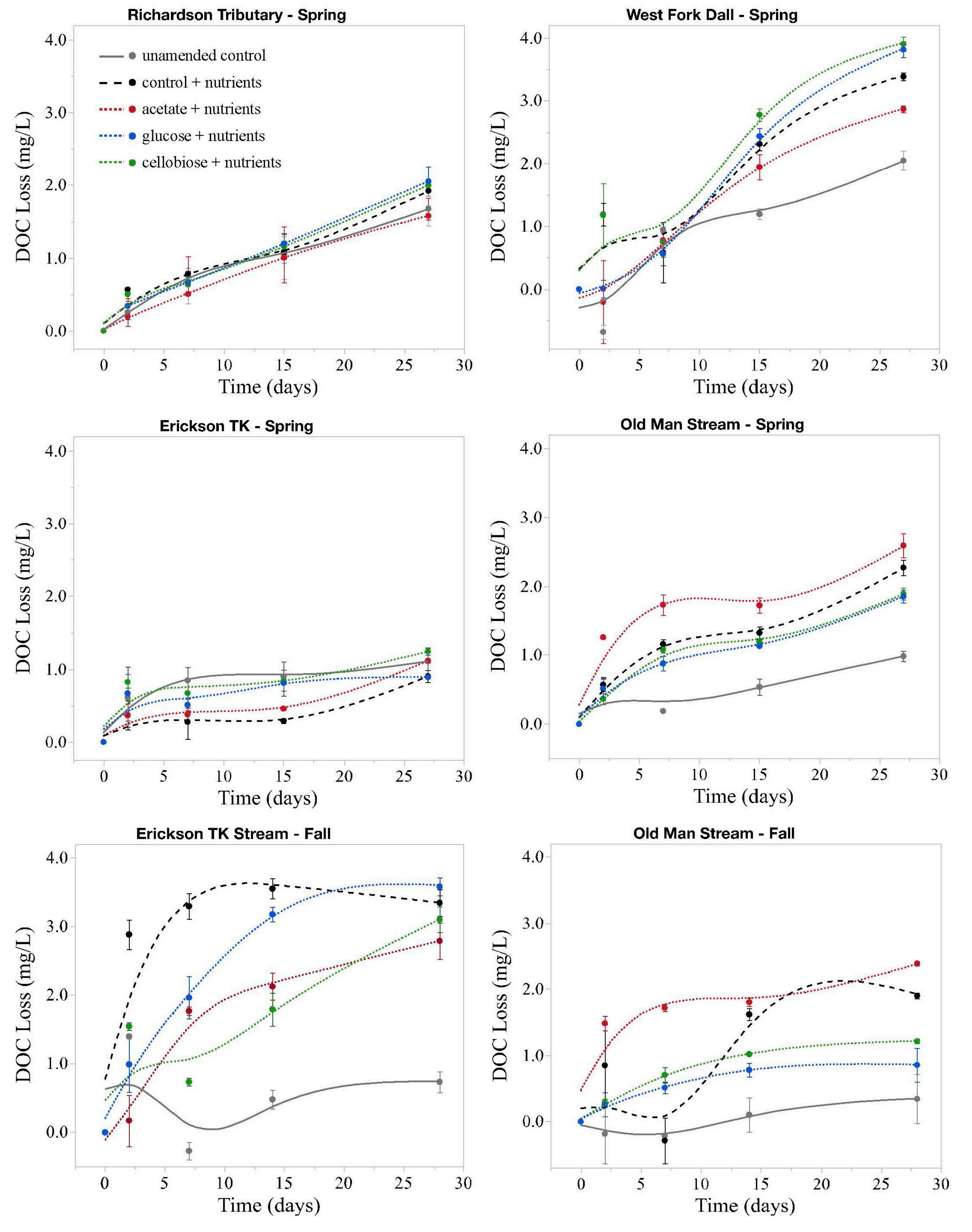

FIGURE 2 | Loss of DOC in microbial incubation experiments. All changes are on the same scale, not exceeding 4 mg L^{-1}. Points are average changes in DOC concentration of the three replicates and bars represent one standard error from the mean. Spring = May; Fall = September.

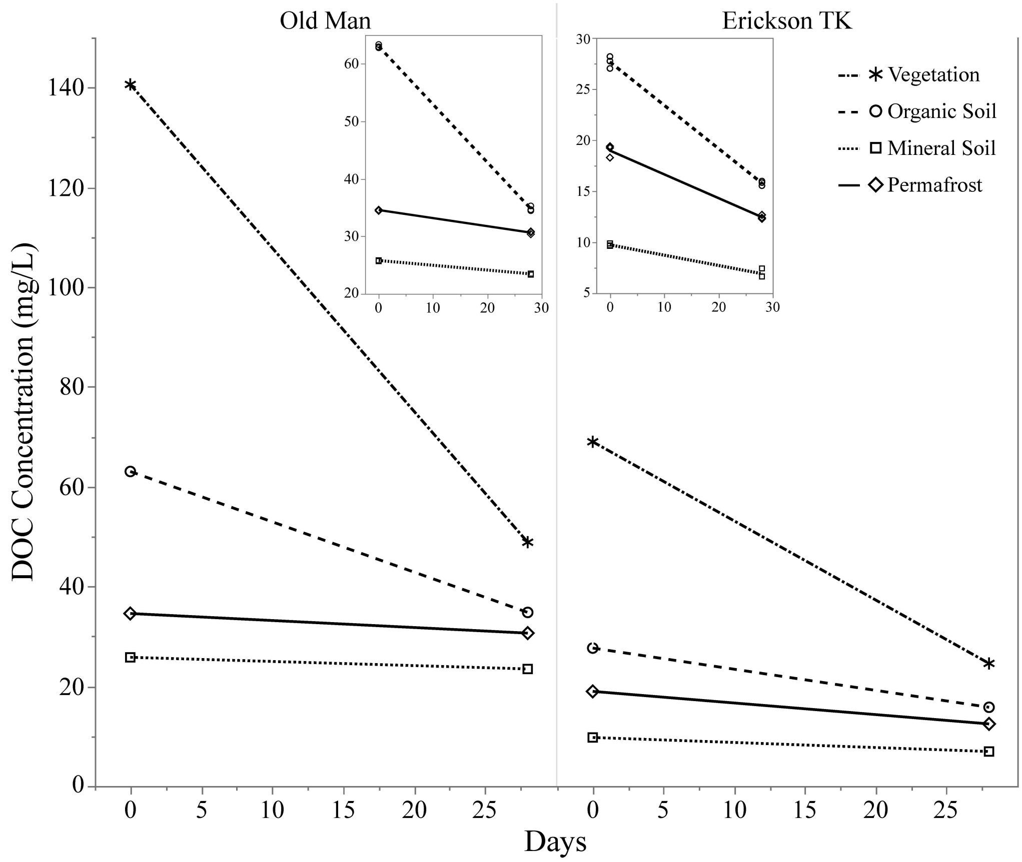

FIGURE 3 | Continuum of dissolved organic carbon (DOC) biodegradability of leachates from different layer types. Compares background DOC loss (i.e., control samples) of layers and two different sites based on DOC concentration at t = 0 and t = 28. Insets show background DOC loss in the soil layers only.

the bioincubation period (**Figure 5**). The relative contribution of polyphenolics and condensed aromatics generally increased but, most notably, there was a large relative decrease in aliphatic compounds in leachate DOM. In permafrost DOM bioincubations, 50–56% of the energy-rich aliphatic compounds were lost over 28 days (**Figure 5**). The other leachate DOM types showed more variability between sites with respect to microbial utilization of aliphatics, with 27–66% loss in vegetation DOM, 25–34% loss in active layer organic soil DOM, and 6–37% loss in active layer mineral soil DOM (**Figure 5**).

Spearman rank correlations of common DOM compounds measured by FT-ICR MS and plotted in van Krevelen space indicated that there is a strong positive correlation between DOM composition and DOC biodegradability ($p < 0.05$; **Figure 6C**). When linear regressions were conducted separately for stream and leachate data, the positive correlation between percent BDOC and relative abundance of aliphatic compounds remained strong for both sample types (streams: $r^2 = 0.79$; $p = 0.008$; leachates: $r^2 = 0.70$; $p = 0.026$; **Figures 6A,B**).

Priming and Nutrient Effects

Priming effects were not evident in any of the stream or leachate bioincubations as there were no significant differences in DOC consumption between the nutrient-amended control and each nutrient- and primer-amended treatment group ($p < 0.05$, Student's t test; **Table 4** and **Figure 2**). Nutrient additions, however, significantly increased DOC consumption in the fall stream bioincubations and the active layer mineral soil leachate bioincubations ($p = 0.003$ and $p = 0.001$, respectively; **Table 4** and **Figure 2**).

DISCUSSION

Vulnerability of Different Dissolved Organic Matter Sources to Microbial Utilization

Dissolved organic matter followed a distinct continuum of biodegradability with respect to both bulk DOC utilization in bioincubation experiments and molecular composition. Stream DOM was relatively stable and resistant to microbial degradation, evidenced by low BDOC values compared to leachate DOM (**Table 2**) and minimal compositional changes during the bioincubation experiments (**Figure 4**). On the other end of the spectrum, vegetation leachate DOM had high

TABLE 3 | Background chemical composition of each DOM source, reflecting the percent of molecular formulae assigned to each compound class (i.e., relative abundance).

DOM Source	Average #MF	Relative abundance (% of molecular formulas assigned)						
		Unsaturated and phenolic (high O/C)	Unsaturated and phenolic (low O/C)	Polyphenolic	Condensed aromatic	Aliphatic	Sugar-like	Peptide-like
Streams (Spring)	4752 ± 2257	52.91 ± 8.28	22.15 ± 2.62	14.82 ± 3.78	5.39 ± 2.08	3.34 ± 0.77	1.24 ± 0.38	0.15 ± 0.18
Streams (Fall)	3148 ± 680	59.24 ± 4.18	21.98 ± 0.66	11.98 ± 2.30	3.40 ± 0.68	2.34 ± 0.22	0.84 ± 0.06	0.22 ± 0.26
Vegetation	3546 ± 1091	41.52 ± 0.86	14.33 ± 1.91	17.07 ± 2.08	7.12 ± 0.39	17.67 ± 0.70	1.45 ± 0.23	0.84 ± 0.28
Organic soil	3677 ± 904	47.45 ± 2.00	16.94 ± 0.60	19.91 ± 2.17	8.72 ± 1.00	5.63 ± 1.36	1.18 ± 0.22	0.16 ± 0.19
Mineral soil	4537 ± 188	41.85 ± 8.24	16.06 ± 1.23	23.93 ± 5.23	13.65 ± 5.69	3.16 ± 0.71	0.94 ± 0.27	0.40 ± 0.47
Permafrost	4652 ± 8	47.84 ± 1.50	14.04 ± 1.99	21.15 ± 0.51	10.32 ± 0.18	5.11 ± 1.33	1.05 ± 0.15	0.51 ± 0.01

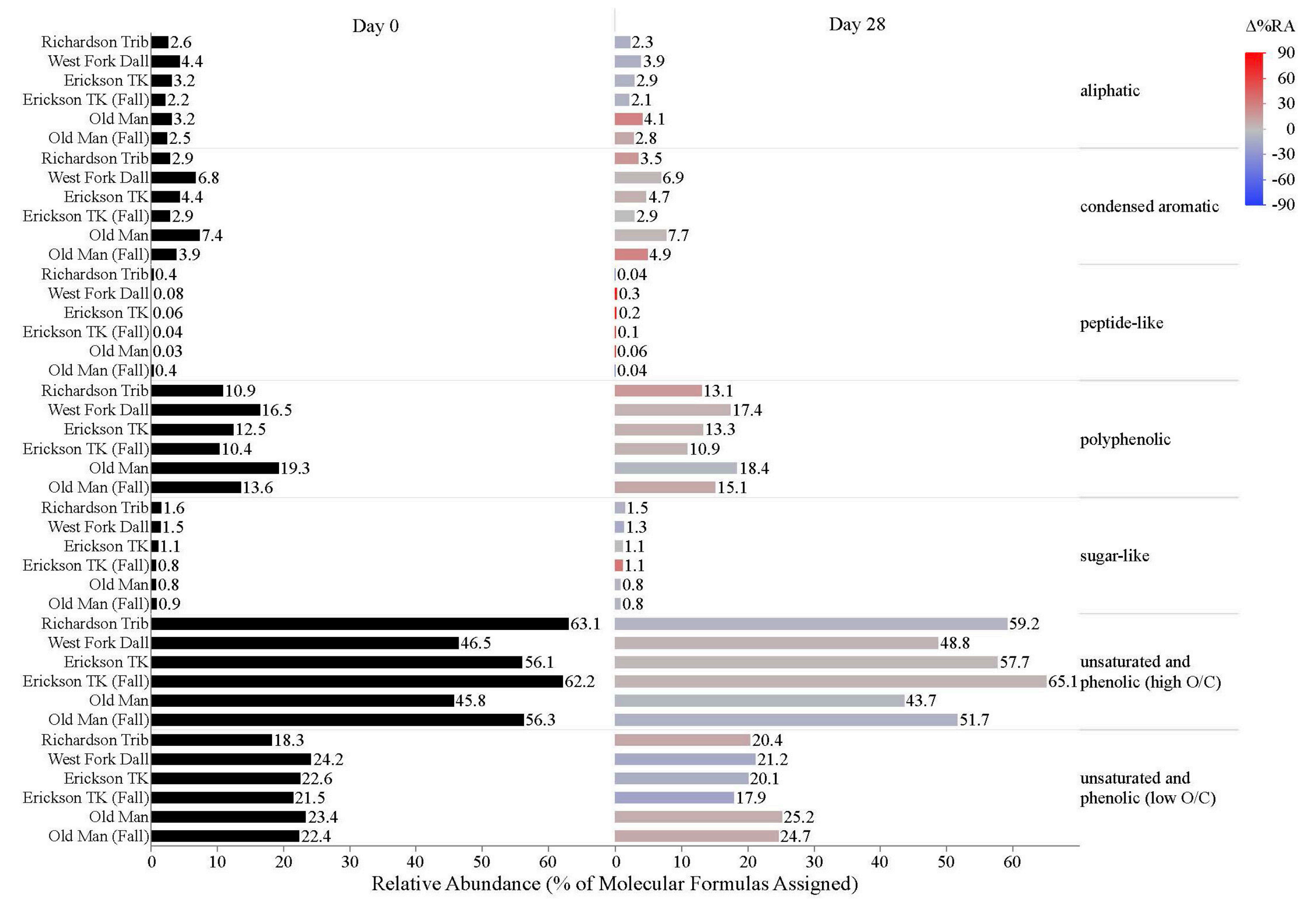

FIGURE 4 | Stream DOM composition by compound class and site. Bars indicate the relative abundance of different compound classes, with black bars showing the relative abundance at $t = 0$ and colored bars representing the relative abundance by $t = 28$. The color scale reflects the percent change in relative abundance of each DOM compound class over the bioincubations, with red bars indicating a relative increase in abundance and blue bars indicating a relative decrease.

BDOC values and higher contributions of energy-rich aliphatic, sugar-like, and peptide-like compounds, and lost up to 66% of aliphatic compounds over the bioincubation experiment (**Table 2** and **Figure 5**). Recent studies have highlighted that elevated contributions of these compounds, particularly aliphatic compounds, are characteristic of highly biolabile DOM (Spencer et al., 2015; Textor et al., 2018).

Mosses dominate inputs to the vegetation leachate and despite the slow decomposition and poor substrate quality of mosses reported by many studies (Hobbie et al., 2000; Hodgkins et al., 2016) they have been shown to leach DOC with high hydrophilic content that is quickly consumed during bioincubations relative to DOC from other vegetation types like black spruce, for example, or fibric and amorphous soil horizons

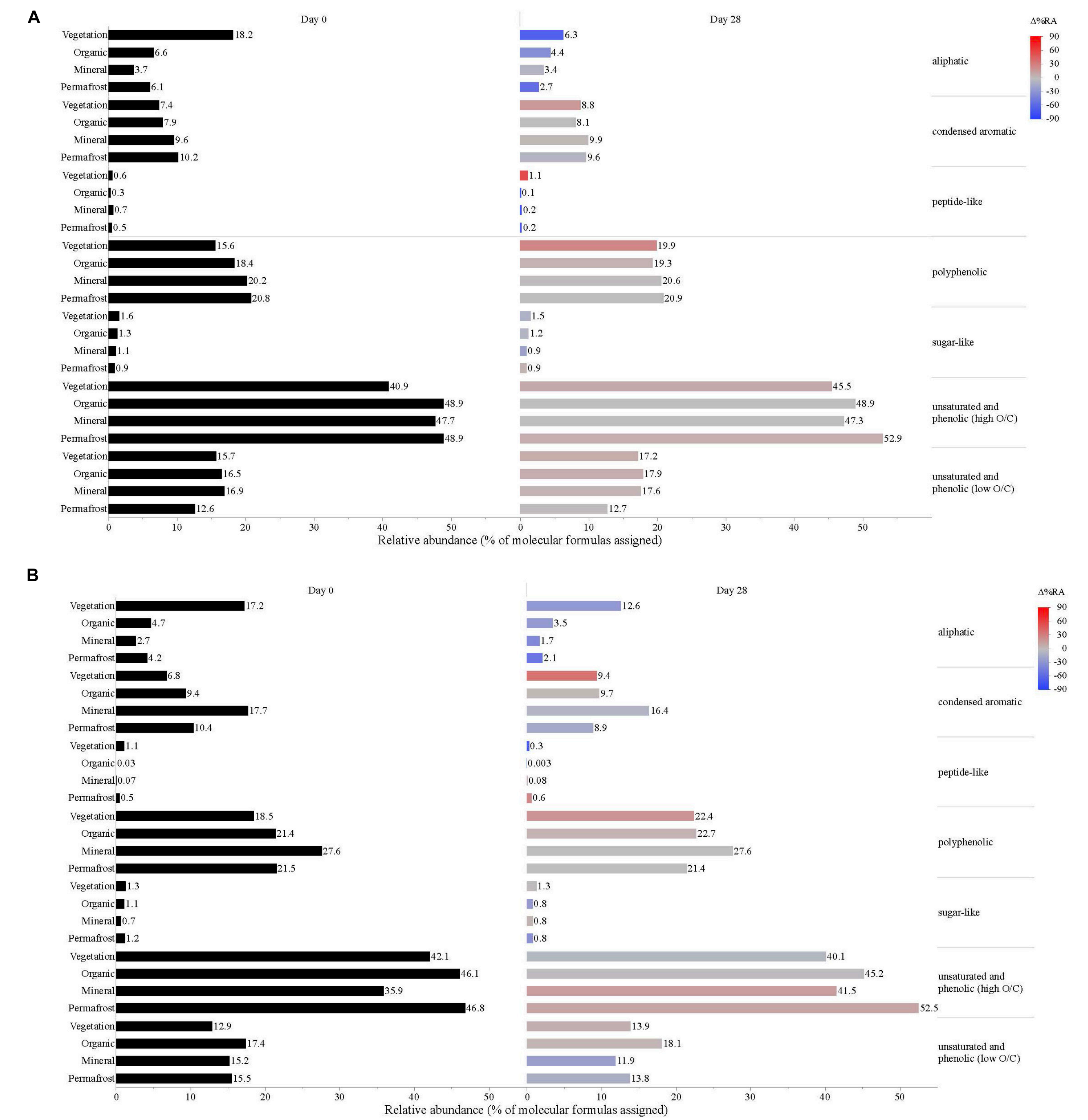

FIGURE 5 | Leachate DOM composition at **(A)** Erickson TK and **(B)** Old Man site by compound class and layer. Bars indicate the relative abundance of different compound classes, with black bars showing the relative abundance at $t = 0$ and colored bars representing the relative abundance by $t = 28$. The color scale reflects the percent change in relative abundance of each DOM compound class over the bioincubations, with red bars indicating a relative increase in abundance and blue bars indicating a relative decrease.

(Wickland et al., 2007; O'Donnell et al., 2016). Considering the high biodegradability of DOM leached from these mosses (Moore and Dalva, 2001; Wickland et al., 2007) and predicted short-term increases in primary productivity (Callaghan et al., 2004), they may represent an increasingly important supply of biolabile DOC to northern high-latitude aquatic ecosystems. Moving deeper into the soil column the biodegradability of active layer organic soil horizons has been shown to be inherently linked to decomposition processes and chemical characteristics of the overlying vegetation (Trumbore and Harden, 1997;

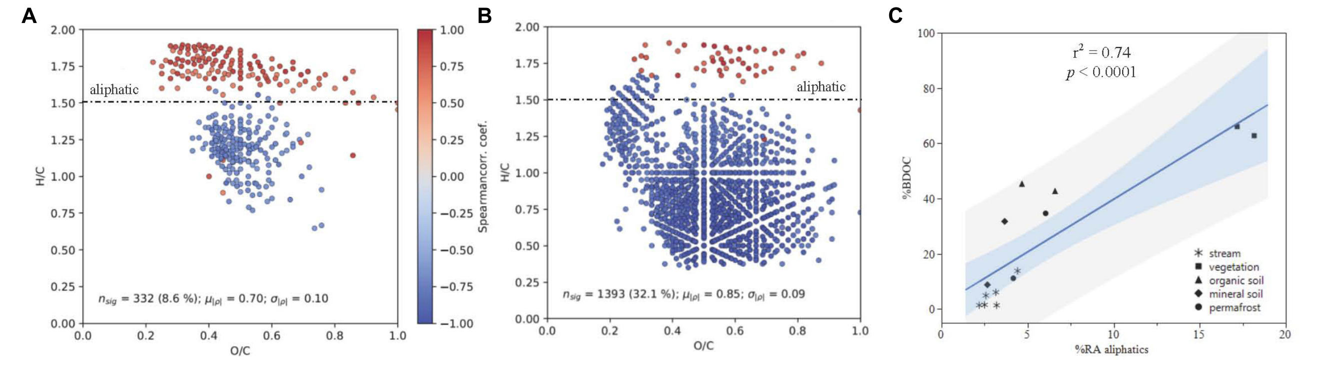

FIGURE 6 | DOM composition as a function of % BDOC plotted in van Krevelen Space for **(A)** all samples and **(B)** leachates only, with the boundary for aliphatic formula assignment displayed (formulas with H/C > 1.50). Points represent molecular formulas measured by FT-ICR MS that were present in >50% of samples and were significantly correlated with % BDOC ($p < 0.05$). Colors indicate the Spearman rank correlation coefficient between the relative intensity of each molecular formula and % BDOC for its associated DOM sample. Red formulas have a higher relative abundance when the proportion of BDOC is high, while blue formulae have a higher relative abundance when the proportion of BDOC is low. **(C)** Shows % BDOC as a function of initial (t = 0) relative abundance of aliphatics ($RA_{ajiphatks}$) all DOM types, where the light blue and gray regions indicate the 95% confidence of fit and prediction, respectively.

TABLE 4 | Reported p-values from Student's t tests to determine significant (a) priming and (b) nutrient effects in streams and leachates.

	One-way ANOVA with Student's t	Spring streams	Fall streams	Vegetation	Organic soil	Mineral soil	Permafrost
		n = 60	n = 30	n = 30	n = 30	n = 30	n = 30
(a) Priming effect	Control plus N + P vs.						
	Aacetate plus N + P	0.8139	0.8098	0.9882	0.9207	0.9364	0.8226
	Glucose plus N + P	0.9488	0.2485	0.6157	0.9190	0.4104	0.5402
	Cellobiose plus N + P	0.7324	0.6323	0.3712	0.8719	0.6246	0.9388
(b) Nutrient effect	Unamended control vs.						
	Control plus N + P	0.0811	0.0030*	0.4385	0.5964	0.0008*	0.0752

*A priming effect would be indicated by a significant difference in DOC consumption between the nutrient-amended control and nutrient- and primer-amended treatments. To test for nutrient effects, DOC consumption in the unamended control and nutrient-amended control were compared. * denotes p < 0.05.*

Jonasson and Shaver, 1999; Jobbagy and Jackson, 2000; Wickland and Neff, 2008; O'Donnell et al., 2011, 2016). Compared to vegetation leachates, DOM from active layer organic soil had greater contributions of polyphenolic and condensed aromatic compounds (**Table 3** and **Figure 5**). However, DOC leached from active layer organic soil was still highly biodegradable (**Table 2** and **Figure 3**) and had high relative abundances of aliphatic and sugar-like DOM compounds that were readily utilized compared to DOM from streams and active layer mineral soils (**Table 3** and **Figures 4**, **5**).

Beneath the active layer organic soil, the DOM leached from the active layer mineral soil was the most resistant to microbial utilization, having the lowest BDOC values out of all the leachate types and exhibiting minimal compositional changes over the bioincubations (**Table 2** and **Figures 3**, **5**). The stability of active layer mineral soil-derived DOM to microbial utilization may be due to high relative contributions of polyphenolic and condensed aromatic compounds (**Table 3** and **Figure 5**) that inhibit the enzyme synthesis or activity necessary for biodegradation (Mann et al., 2014), as well as sorption processes that are highly prevalent in mineral soils (Kalbitz et al., 2000). Mineral soils have been shown to preferentially adsorb higher molecular weight DOM fractions (Gu et al., 1995; Kalbitz et al., 2000) and hydrophobic acids (Qualls and Haines, 1992), which are less biologically available. It is also likely that the stability of DOM to microbial degradation increases as it is adsorbed to mineral surfaces (Kalbitz et al., 2000). In accordance with our finding that active layer mineral soil DOM was the least biodegradable of the soil layers analyzed, it had the lowest relative contribution of aliphatic compounds (**Table 3** and **Figure 5**).

The type of permafrost under study has been shown to impact the biolability of exported organic matter (Kawahigashi et al., 2004; Schuur et al., 2008; Wickland et al., 2018). For example, Pleistocene-aged yedoma permafrost is widespread throughout Alaska and Siberia and releases extremely biolabile DOC upon thaw (Holmes et al., 2012; Vonk and Gustafsson, 2013; Abbott et al., 2014; Drake et al., 2015; Mann et al., 2015; Spencer et al., 2015; Vonk et al., 2015). As much as 65% of DOC from yedoma thaw is utilized within 30–40 day bioincubation experiments (Vonk et al., 2015) and a study by Spencer et al. (2015) revealed that up to >90% of aliphatic molecular formulae in DOM from Siberian yedoma thaw streams were utilized within 28 days. Past studies have also shown distinct differences in biolability between permafrost in continuous versus discontinuous permafrost regions (Kawahigashi et al., 2004; Vonk et al., 2015). In this study focused on discontinuous permafrost regions, we saw up to 34% loss of permafrost DOC and up to 56% loss of energy-rich aliphatic molecular formulae in permafrost DOM (**Table 2** and **Figure 5**). While continuous permafrost regions contain preserved, unique DOC that is highly susceptible to microbial degradation (Kawahigashi et al., 2004), discontinuous permafrost regions are warmer and typical contain more aqueous environments allowing for microbial processing, and may have experienced previous leaching or microbial decomposition (Kawahigashi et al., 2004; Schuur et al., 2008; Vonk et al., 2015). This may explain the relatively lower loss of DOC and energy-rich aliphatic molecular formulae versus that observed in previous studies focused in continuous permafrost regions. However, it should be noted the permafrost in this study region still showed higher DOC loss than that of overlying active layer mineral soils and adjacent streams.

Role of Chemical Composition on the Fate of Dissolved Organic Matter

A warming climate will potentially change the chemical nature and fate of DOM draining from areas underlain by permafrost (Dittmar and Kattner, 2003; Mann et al., 2012; Ward and Cory, 2015; O'Donnell et al., 2016; Wickland et al., 2018), which has implications for aquatic carbon cycling in these regions. DOM is an extremely diverse mixture of substances (Thurman et al., 1985; Nebbioso and Piccolo, 2013) that, when characterized, can provide insight into DOM biodegradability (Sun et al., 1997; Spencer et al., 2008; Wickland et al., 2012; Zhang et al., 2017). By utilizing FT-ICR MS analysis, we were able to assess the link between underlying DOM composition and biodegradability at the molecular level. Further, by comparing DOM composition at the initial and final time points in bioincubation experiments, FT-ICR MS analysis allowed us to assess which compounds were susceptible to microbial utilization.

We observed that DOM composition from both streams and various terrestrial sources followed a distinct pattern of biodegradability. While stream DOM was relatively stable and experienced minor DOM compositional changes during the bioincubations, the DOM that would naturally be released into streams from vegetation and soils was typically more bioavailable and exhibited greater compositional changes. This pattern agrees strongly with previous findings that the biodegradability of DOM tends to decrease along a soil-stream-river continuum (Battin et al., 2008; Fellman et al., 2014; Mann et al., 2015; Spencer et al., 2015; Hutchins et al., 2017).

The positive correlation between DOM composition and DOC biodegradability was largely driven by the contribution of aliphatic compounds ($H/C \geq 1.5$, $O/C < 0.9$) to DOM composition (**Figure 6**). Concurrent with these findings, consistent reductions in the relative abundance of aliphatic compounds over the bioincubations measured by FT-ICR MS indicate that these molecular formulae were preferentially utilized by stream microbes, which has been observed in other studies (Spencer et al., 2015; O'Donnell et al., 2016). Additionally, aliphatics had smaller relative contributions to the DOM pool sourced from deeper organic soil layers, which has been attributed to preferential microbial utilization of low molecular weight compounds (Drake et al., 2015; Spencer et al., 2015).

Contrarily, the relative abundance of polyphenolic and condensed aromatic compounds increased with soil depth, which has been previously reported for FT-ICR MS analysis of organic soils in boreal regions (O'Donnell et al., 2016) and suggests that these aromatic compounds are preferentially preserved with depth in organic soil horizons. Polyphenolic compounds are largely derived from vascular plant material, especially in boreal systems (Kellerman et al., 2015), while condensed aromatics are terrigenous combustion-derived compounds (Hockaday et al., 2006; Kellerman et al., 2018). The higher relative contribution of polyphenolic compounds with depth in DOM from organic soil horizons is likely due to the preferential preservation of vascular plant material from which polyphenols are derived (O'Donnell et al., 2016) and inhibitory effects of polyphenolic DOM content on biodegradation (Mann et al., 2014). Although the relative abundance of polyphenolics and condensed aromatics generally increased over the bioincubation period, consistent with their known stability to microbial degradation (Kim et al., 2006; Jaffé et al., 2013; O'Donnell et al., 2016; Kellerman et al., 2018), changes in relative abundance were generally small (**Figure 5**). We also observed an increase in the number of molecular formula assignments with depth (**Table 3**), indicating that deeper soil layers likely export DOM with greater chemodiversity (Zhang et al., 2017; Zark and Dittmar, 2018). Based on these findings, chemical composition of DOM, particularly the contribution of aliphatics, appears to be a major control on microbial respiration in boreal discontinuous permafrost regions.

No Priming Effect in Permafrost-Influenced Watersheds

This study is to the best of our knowledge the first to investigate the potential role of priming in northern high-latitude, permafrost-influenced watersheds. Out of the 18 different treatments of stream and leachate samples amended with OC substrates, none showed a significant priming effect ($p < 0.05$, Student's t test, **Table 4**). The addition of simple OC substrates did not invoke a significant change in the amount of DOC consumed over 28 days (**Table 4** and **Figure 2**), indicating that priming appears to play no role in altering DOC turnover in these regions.

The timescale over which priming is measured is important when considering the quantitative relevance of priming with respect to DOC mineralization and CO_2 fluxes from aquatic ecosystems. Many aquatic studies on the priming effect that have reported evidence of priming describe the phenomenon as "apparent" or "transient" because, although they observed initial differences in DOC consumption between unamended and primed treatments, ultimately the amount of DOC consumed after about 1 month is not significantly different from background consumption (Steen et al., 2016; Textor et al., 2018).

An apparent priming effect occurs when microbial biomass turnover is affected, but not OM decomposition (Blagodatskaya and Kuzyakov, 2008; Kuzyakov, 2010). However, a real priming effect is evidenced by OM mineralization rates that are higher than ambient rates, resulting in the decomposition of more stable OM (Jenkinson et al., 1985). Studies that utilize isotopic labeling and modeled decay rates to study priming (Koehler et al., 2012; Bengtsson et al., 2014; Hotchkiss et al., 2014; Ward et al., 2016) can trace the degradation of biolable and biostable pools separately. While it is possible that priming may increase the rate of DOC mineralization initially in a triggering effect (Blagodatskaya and Kuzyakov, 2008), the quantitative importance of such priming effects in the long term may be limited (Steen et al., 2016; Ward et al., 2017; Textor et al., 2018). Thus, such studies that measure priming based on short-term modeled decay rates may overestimate the importance of priming.

We recognize that our pragmatic approach to assessing the priming effect through simple biodegradation experiments makes it difficult to distinguish between turnover of stable and biolabile DOC pools. However, throughout extensive replication, the amount of DOC consumed was statistically the same in the control and primed treatments after 28 day long bioincubations when the majority of BDOC has been respired (Wickland et al., 2007; Vonk et al., 2015). Therefore, we have no reason to believe that the stable DOC pools in the primed treatments were more susceptible to biodegradation than in the controls. Additionally, natural DOC in aquatic systems does not necessarily fall into "biolabile" or "stable" categories; rather, any given DOC pool is constantly evolving along the aquatic continuum and consists of multiple sub-pools of different ages and reactivities (Mostovaya et al., 2017; Vachon et al., 2017), presenting another challenge to assessing the priming effect.

A number of studies have shown that inorganic nutrient availability is strongly correlated to DOC biodegradability in arctic and boreal systems (Holmes et al., 2008; Wickland et al., 2012; Mann et al., 2014), while others have found that BDOC is unresponsive to inorganic nutrient additions (Abbott et al., 2014; Mann et al., 2015; Vonk et al., 2015). In this study, nutrient limitation in samples was evident for the fall stream and active layer mineral soil leachate DOC bioincubations, in which we found a significant difference between the percent of BDOC in the unamended and nutrient-amended samples ($p < 0.05$, Student's t test; **Table 4**). Stream samples collected during fall had relatively high DOC concentrations and low proportions of BDOC (**Table 2**), as microbial metabolism was likely limited by naturally occurring stoichiometric constraints on inorganic nutrient availability in the Yukon River Basin during fall (Wickland et al., 2012). However, "primed" samples amended with nutrients and simple OC substrates, were not significantly different from the nutrient-amended control (i.e., no priming; $p < 0.05$, Student's t test; **Table 4**). While many studies use algal or macrophyte exudates as primers (Danger et al., 2013; Attermeyer et al., 2014; Bengtsson et al., 2014; Hotchkiss et al., 2014; Ward et al., 2016), these sources of biolabile autochthonous OC also contain nutrients that may stimulate biodegradation, confounding the effect of added OC substrates on OM degradation with nutrients. The use of simple OC substrates and separate controls (i.e., with and without nutrients) ensures that priming can be measured separately from the confounding effect of nutrients (Textor et al., 2018). DOM turnover in response to biolabile OC inputs ultimately depends upon nutrient availability, which is also tightly coupled to microbial growth efficiencies (del Giorgio and Cole, 1998; Smith and Prairie, 2004; Franke et al., 2013). Thus it is critical to establish a clearer distinction between priming and the underlying mechanisms, such as nutrient stoichiometry and microbial activity, involved in DOM turnover in aquatic ecosystems.

The extent to which priming alters DOC cycling on a quantitatively relevant scale remains uncertain and, in permafrost-influenced watersheds, seems unlikely to play a major role. Bengtsson et al. (2018) recently conducted the most extensive meta-analysis of aquatic priming studies to date, including a variety of ecosystems along the aquatic continuum. By calculating log response ratios of mean OC degradation values for primed and control treatments to estimate the magnitude of priming effects, they found that a mean priming effect was not significantly different from zero across quantitative studies, with streams falling below the overall average (Bengtsson et al., 2018). Although DOM degradation rates are not likely altered by priming in various aquatic ecosystems, DOM molecular properties and underlying microbial processes hold promise in understanding some of the knowledge gaps in DOM turnover in the aquatic sciences. While this study is the first to investigate the potential of priming in northern high-latitude, permafrost-influenced watersheds, continued research will help develop a consensus on the role of priming in these dynamic systems.

Implications and Future Directions

Climate change and associated increases in permafrost thaw have implications for the quantity and biolability of DOC exported to and from streams and rivers in boreal and arctic regions (Vonk et al., 2015). Increasing thaw depth due to warming will release relatively preserved material from deeper soil layers that increases the amount of DOM available for microbial respiration, and has implications for stream DOM composition (Drake et al., 2015; O'Donnell et al., 2016; Wickland et al., 2018). This and other recent studies suggest that the chemical composition of DOM, especially aliphatic content, can be a good predictor of biodegradability (**Figure 6**) when examining permafrost draining watersheds and that permafrost-derived DOM is typically more susceptible to biodegradation than active layer mineral soil derived DOM in the same region.

While priming does not appear to be an important mechanism for increasing DOC turnover in boreal, discontinuous permafrost regions, the mobilization of inorganic nutrients from thawing permafrost may be important for alleviating nutrient constraints on microbial remineralization of DOC (Wrona et al., 2006; Holmes et al., 2012; Wickland et al., 2012). Permafrost thaw waters contain relatively high concentrations of inorganic nutrients (Tarnocai et al., 2009; Keuper et al., 2012; Abbott et al., 2014; Harms et al., 2014), and microbial metabolism in northern high-latitude aquatic ecosystems is often limited by inorganic nutrient availability (Dittmar and Kattner, 2003; McClelland et al., 2007; Holmes et al., 2008, 2012; Wickland et al., 2012). As seen in this study, inorganic nutrient additions can enhance DOC mineralization (**Figure 2** and **Table 4**). Thus the concurrent release of biolabile permafrost DOC and inorganic nutrients with future warming in northern high-latitudes may enhance stream respiration by alleviating nutrient limitation (Striegl et al., 2005; Wrona et al., 2006; Wickland et al., 2012; Abbott et al., 2014; Harms et al., 2014; Mann et al., 2014) which may contribute to the predicted increases in greenhouse gas emissions from aquatic ecosystems in permafrost regions (Christensen et al., 2004; Schuur et al., 2009; Settele et al., 2014). Finally, results from this study suggest that priming of DOC derived from streams, vegetation, and soils across a variety of sites underlain by discontinuous permafrost seems unlikely due to the limited response of these DOC sources when amended with biolabile OC substrates. Therefore, it seems apparent that addition of biolabile permafrost DOM to aquatic ecosystems in northern high-latitude regions will not further prime turnover of relatively modern, more stable DOM sources, and thus future projections of carbon turnover in streams can be linked directly to permafrost thaw within the watersheds.

AUTHOR CONTRIBUTIONS

RS, ST, and KW conceived the study and provided the materials. ST, KW, and SJ conducted the fieldwork. ST, DP, and SJ carried out the laboratory analyses in support of this study. ST drafted the initial manuscript. KW and RS edited extensively. All authors read and contributed to the final version of the manuscript.

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