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Biogeosciences Discussions

Age and Chemistry of Dissolved Organic Carbon Reveal Enhanced Leaching of Ancient Labile Carbon at the Permafrost Thaw Zone

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Abstract. Climate change will alter the balance between frozen and thawed conditions in Arctic systems. Increased temperatures will make the extensive northern permafrost carbon stock vulnerable to decomposition and translocation. Production, cycling, and transport of dissolved organic carbon (DOC) are crucial processes for high-latitude ecosystem carbon loss that result in considerable export off the Arctic landscape. To identify where and under what conditions permafrost DOC is mobilized in an Arctic headwater catchment, we measured radiocarbon (^{14}C) of DOC and assessed DOC composition with ultraviolet-visible spectroscopy (UV-vis), of surface waters and shallow and deep subsurface pore waters from 17 drainages in the Barrow Environmental Observatory in Alaska. Samples were collected in July and September 2013 to assess changes in age and chemistry of DOC over time. DOC age was highly variable ranging from modern (19 ‰ $\Delta^{14}C$) to approximately 7000 y BP (-583 ‰ $\Delta^{14}C$). DOC age increased with depth, over the summer as the active layer deepened, and with increasing drainage size. DOC quality indicators reflected a DOC source rich in high-molecular weight and aromatic compounds throughout the summer and a weak relationship with DOC age. In deep porewaters, DOC age was also correlated with several biogeochemical indicators, suggesting a coupling between carbon and redox biogeochemistry influencing methane production. In the drained thawed lake basins included in this study, DOC concentrations and contributions of vegetation-derived organic matter declined with increasing basin age. The weak relationship between DOC age and chemistry and consistency in DOC chemical indicators over the summer suggest high lability of old DOC released by thawing permafrost.

1 Introduction

Soils of the northern permafrost region store nearly 1700 Pg of organic carbon (Tarnocai et al., 2009; Schuur et al., 2008). This extensive carbon pool is vulnerable to climate change as warmer temperatures increase thawing, microbial decomposition, fire frequency, and erosion (Schuur et al., 2013; Schuur et al., 2008). Loss of this permafrost carbon to the atmosphere poses a considerable potential feedback to climate change (Schaefer et al., 2014; Koven et al., 2011), with an

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estimated 5–15% of permafrost soil carbon projected to be released to the atmosphere by the end of this century under the current warming trajectory (Schuur et al., 2015).

Carbon mobilized from thawing permafrost and warmer active-layer soils may be microbially transformed into carbon dioxide (CO_2) or methane (CH_4), which can be emitted directly to the atmosphere (Schadel et al., 2016; Hicks Pries et al., 2013). Less well-studied than these direct fluxes to the atmosphere (Vonk et al., 2019), dissolved organic carbon (DOC) provides the carbon source for microbes and the subsequent production of gaseous fluxes (Charman et al., 1999; Chanton et al., 2008; Molot and Dillon, 1997; Corbett et al., 2013; Shirokova et al., 2013). Crucially, DOC also has the potential to be transported, potentially off the landscape through drainages, streams, and ultimately export to the ocean (Raymond et al., 2007; Holmes et al., 2011; Cole et al., 2007). Lateral transport of dissolved carbon is a crucial mechanism for terrestrial carbon loss in the Arctic and results in an export off the landscape of up to 25% of net ecosystem productivity (calculated from Mcguire et al., 2009), exceeds net ecosystem exchange of carbon in some northern ecosystems (Aurela et al., 2002; Billett et al., 2004; Christensen et al., 2007; Roulet et al., 2007), and at the global scale is comparable in magnitude to the land and ocean CO_2 sinks (Drake et al., 2018a; Tank et al., 2018).

DOC accounts for much of this carbon loss (Billett et al., 2004; Mcguire et al., 2009; Mcclelland et al., 2016), and several studies have reported ancient radiocarbon ages for DOC in rivers, including 2000–500 yBP in erosion-impacted streams in the Kolyma River Basin (Mann et al., 2015) to over 20,000 yBP in streams freshly formed from thawing ice-rich Yedoma permafrost (Vonk et al., 2013). Furthermore, research shows that a substantial portion of this DOC (20–50%) is labile (Mann et al., 2012; Mann et al., 2015; Holmes et al., 2008; Liu et al., 2019) and may be decomposed and released back to the atmosphere as CO_2 or CH_4 from soils, surface waters, or drainages (Kling et al., 1991; Cole et al., 2007; Drake et al., 2015). In fact, increasing terrestrial DOC loads have been linked to increased CO_2 emissions from aquatic systems (Lapierre et al., 2013).

The combination of melting permafrost, vegetation changes, increased snowfall and subsequent snowmelt is likely to result in an increase in the role of DOC as a mode of carbon transport within and across the Arctic landscape (Frey, 2005; Finlay et al., 2006; Kawahigashi et al., 2004). How the production and fate of terrigenous DOC will respond to future climate change is not well constrained. Studies suggest that increasing temperature increases DOC production along with soil carbon

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decomposition (Neff and Hooper, 2002; Freeman et al., 2001). Increased DOC production is also expected as permafrost melts, active layers deepen, and shrub encroachment occurs (Frey and Mcclelland, 2009). However, numerous studies have shown that the fate of DOC is highly dependent on hydrology (Pastor et al., 2003; Kellerman et al., 2019; Raymond et al., 2016). Specifically, in wet years or in cases where hydrologic flow paths facilitate lateral movement of DOC to surface waters, warming may increase DOC production, loss from terrestrial ecosystems, and export to surface waters (Freeman et al., 2001). This seems to be the current case for the Arctic as DOC export by streams and rivers increases with increasing streamflow, implying that DOC transport and production is water, not carbon, limited (Finlay et al., 2006; Raymond et al., 2007; Guo and Macdonald, 2006; Guo et al., 2007; Townsend-Small et al., 2011; Prokushkin et al., 2011). However, in drier conditions or when flow to surface waters is slow, DOC produced in soil and peat may be decomposed in situ, increasing soil and ecosystem CO_2 and CH_4 fluxes to the atmosphere (Pastor et al., 2003). Alternatively, DOC may move down the soil profile where it may interact with mineral soils and be sorbed, stabilized, or remineralized to CO_2 or CH_4 (Fan et al., 2010; Frey and Mcclelland, 2009) and could provide a priming effect for decomposition of old carbon stores (Fan et al., 2010; Hayes et al., 2014; Wild et al., 2014).

Radiocarbon analyses and characterization of DOC provide insights into the sources, transfer, and lability of DOC from arctic and subarctic ecosystems (Olefeldt and Roulet, 2012; Benner et al., 2004; Raymond et al., 2007; Guo and Macdonald, 2006; Amon and Meon, 2004) and can therefore provide crucial information about mechanisms behind carbon loss and transport that is not currently captured appropriately in high-latitude models. Large stores of inert yet labile permafrost carbon have, as a function of age, a unique ^{14}C-isotopic signature that follows the carbon into the DOC pool. For example, very high concentrations of old DOC ($\geq$ 20 ky) have been observed in streams with drainage basins encompassing thawing Yedoma permafrost, demonstrating that actively thawing systems are, in fact, releasing large amounts of old, previously frozen carbon (Vonk et al., 2013). Furthermore, seasonal patterns of DOC loadings and ^{14}C-age of DOC in arctic rivers exhibit a nearly consistent pattern with high concentrations of young (i.e., recently fixed) DOC following spring thaw, and slightly lower concentrations of DOC with an older ^{14}C-age associated with baseflow (Guo and Macdonald, 2006; Guo et al., 2007; Raymond et al., 2007; Striegl et al., 2007; Neff et al., 2006; Amon et al., 2012; Wild et al., 2019).

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The molecular chemistry and biolability of DOC exported by large Arctic streams and rivers also change seasonally. High flows associated with spring thaw contain higher amounts of relatively labile, vegetation and litter-derived DOC, but as streamflow decreases, DOC becomes both older and more depleted in compounds associated with vegetation inputs (Finlay et al., 2006; Neff et al., 2006; Holmes et al., 2008; Prokushkin et al., 2011; Striegl et al., 2007). For example, in large Arctic rivers, assessments of DOC optical properties have indicated higher aromaticity, lignin phenol concentrations, and molecular weights associated with high flows during snowmelt (Spencer et al., 2008; Mann et al., 2016) and declines in aromaticity between summer and winter (O'donnell et al., 2012). A similar decline in aromaticity, assessed with ultraviolet-visible spectroscopy (UV-vis), of DOC in the Kolyma River and its tributaries from spring to late summer coincided with a decline in DOC ^{14}C values (Neff et al., 2006). Furthermore, a pan-Arctic study of DOC biodegradability assessed with incubations observed declines in biodegradability of DOC in large streams and rivers over the year (from January to December), likely attributable to shifts in DOC source and hydrologic residence times as small streams and soil leachates showed no seasonal trends in the biolability of DOC (Vonk et al., 2015a).

The extent of permafrost thaw in Arctic watersheds also impacts DOC content and biolability in streams and rivers. In the pan-Arctic study listed above, continuous permafrost yielded higher amounts and lability of DOC in soil leachates than areas with discontinuous permafrost as assessed in laboratory incubations (Vonk et al., 2015a). Similarly, in the North Slope of Alaska, rivers in watersheds with continuous permafrost had lower DOC concentrations with higher amounts of aliphatic compounds (indicative of microbial processing), while watersheds with more extensive permafrost thaw yielded DOC with characteristics indicative of unprocessed vegetation-derived organic matter including higher relative amounts of aromatics, polyphenols, and lignin (Johnston et al., 2021) .

The information gained from stream water samples is valuable, but these streams integrate processes across the landscape and do not provide information about the locations within their watersheds where older or more labile C is being mobilized, limiting our ability to attribute these observations to processes. Yet, small watersheds and headwater streams remain understudied relative to large river basins (Vonk et al., 2015b; Shogren et al., 2019) even though these headwater catchments release DOC that is older and more biodegradable than larger rivers further along fluvial networks (Vonk et al., 2015a; Coch et al., 2019; Drake et al., 2018b; Textor et al., 2019). To bring us closer to identifying the conditions and processes influencing

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105 the production and transport of permafrost-derived DOC in headwater Arctic catchments, we measured DOC age (^{14}C) and chemistry of surface waters and soil porewaters in a survey of 17 drainages with different characteristics in the Barrow Environmental Observatory, Alaska. We integrate these new data (^{14}C of DOC and UV-vis) with previously published biogeochemical tracers from the same sampling campaign (Throckmorton et al., 2015b) to elucidate the mechanisms behind DOC cycling across these drainages. This approach addresses some of the current challenges in this area of research by 110 providing field implementation of biogeochemical tracers that can be used to infer changes in DOC cycling (Vonk et al., 2019). We hypothesized that in most drainages, DOC would become older and more enriched in aromatics and high molecular weight compounds over the course of the summer as active layers deepened, exposing organic matter that had not been microbially processed. We also expected to find spatial patterns in DOC age and chemistry reflecting differences in drainage characteristics such as a shift toward DOC sourced from older, more processed soil organic matter in older drained thaw lake basins as well 115 as with increasing catchment size.

2 Materials and Methods

2.1 Study Area and Field Sampling

The study area and sample collection have been described previously (Throckmorton et al., 2015b). Briefly, surface and pore water samples were collected in July and September of 2013 from 17 drainages in and around the Barrow 120 Environmental Observatory on the Arctic Coastal Plain near Utqiavik, Alaska (71.3°N, 156.6°W, Fig. 1). Sampling locations were along the periphery of internal and external drainages that included drained thaw lake basins of differing age, interlake basin areas, and different types of polygonal terrain. Sampling locations further classified by water flow, either "stagnant" wetlands (no observable flow during sampling) or "gentle flow" (channels with gentle lateral surficial flow was observed during sampling), although samples were collected from areas that appeared stagnant prior to sampling. Samples were collected 125 from three depths at each location: surface water, shallow subsurface soil porewater, and deep subsurface soil porewater. Grab samples were collected from surface waters at the edges of drainages. Shallow porewaters were collected with stainless steel drive points from 7.5–15 cm below the surface, which was typically organic soil. Deep porewaters were collected with macro-rhizon samplers from the maximum depth to the frost table, which ranged from 27–64 cm below the surface and varied across

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sites and sampling month (34 cm in July and 43 cm in September, on average). Samples were filtered in the field through 0.45 or 0.2 μm Fisherbrand nylon syringe filters, depending on the analyte of interest (see below).

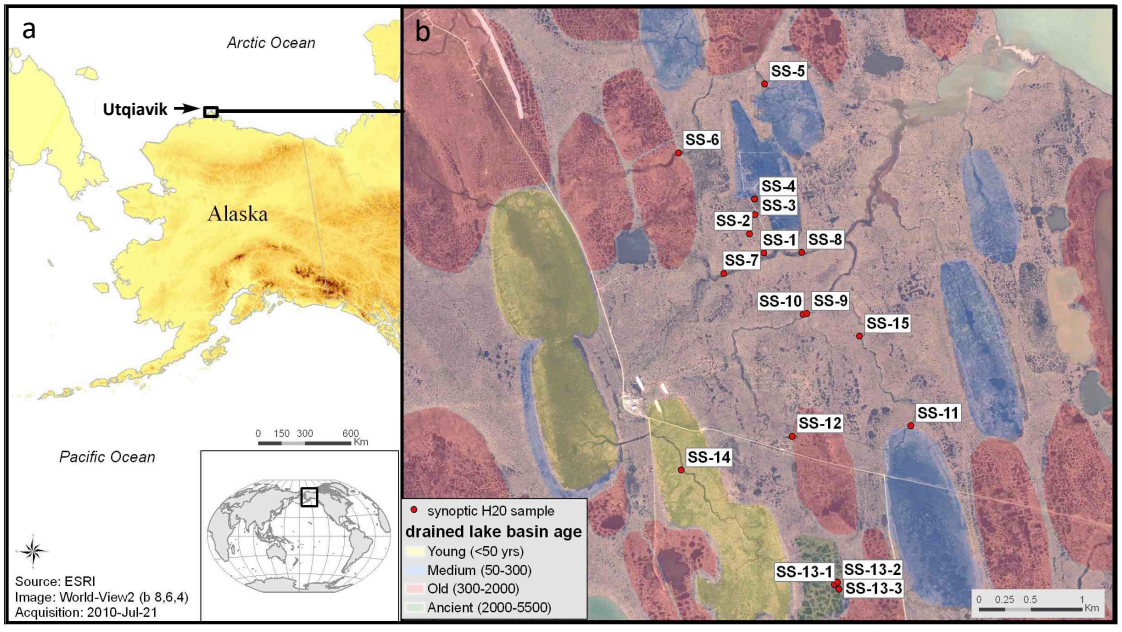

Figure 1: Location of Utquivik, Alaska, USA (a) and water sampling sites (b). Colours in (b) indicate different aged drained thaw lake basins (DTLB); see inset legend for ages (Hinkel et al., 2003). Reproduced from Throckmorton et al. (2015a).

2.2 Surface and Soil Pore Water Measurements

The chemistry of DOC was assessed based on spectral properties with UV-Vis absorbance (of samples filtered in the field through 0.45 μm Fisher syringe filters) at room temperature (quartz tube; 1 cm path) at Los Alamos National Laboratory. Absorbance at 254, 350, and 440 nm were selected as spectral wavelengths of interest as they have been shown to correlate strongly with DOC concentration in rivers, particularly in those dominated by terrestrial organic matter inputs (Spencer et al., 2012). Absorption coefficients were calculated following Eq. (1):

$$\alpha_\lambda = \frac{2.303 * A_\lambda}{l}, \quad (1)$$

where A_λ is spectral absorbance at a specific wavelength (λ) and l is the cell path length in m. We observed that absorption coefficients for all 3 wavelengths of interest positively correlated with DOC concentration ($p < 0.01$). Therefore, we weighted

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the absorbance coefficients by DOC concentration (in mg L^{-1}) for further statistical analysis of carbon-specific ultraviolet absorbance (SUVA) in L mgC^{-1} m^{-1} for the targeted wavelengths as has been done by others previously (Weishaar et al., 2003). Some samples had absorbance less than the blank at 350 and 440 nm and were set to zero for further statistical analysis. SUVA values for 3 samples with DOC concentrations below 3 mg L^{-1} were removed as outliers because low DOC concentrations yielded very high SUVA values (1–2 orders of magnitude higher than the other samples).

Of the 102 total water samples collected, 80 had enough sample (0.45 μm-filtered and stored in amber glass vials) after other analyses to send to Lawrence Livermore National Laboratory for radiocarbon analysis. Samples were freeze dried, treated with 1N HCl at 70°C to remove residual carbonate, and dried at 70°C to remove acid without rinsing. Samples were then combusted to CO_2 and reduced to graphite onto Fe powder in the presence of H_2 (Vogel et al., 1984). Measured $\delta^{13}C$ values were used to correct for mass-dependent fractionation and ^{14}C values are reported as $\Delta^{14}C$ (‰) corrected to the year of measurement, either 2016 or 2017 (Stuiver and Polach, 1977).

A suite of biogeochemical indicators was analysed on these samples with results presented previously (Throckmorton et al., 2015b). These analytes add to the interpretation of the new data presented in this paper (^{14}C of DOC and SUVA). Briefly, samples were analysed in the field for Fe^{2+}, temperature, DO, and pH. Samples were analysed at Los Alamos National Laboratory for concentrations and $\delta^{13}C$ of dissolved CH_4 and DIC (from samples filtered in the field through 0.2 μm Fisher syringe filters), for concentrations and $\delta^{13}C$ or $\delta^{15}N$ of DOC and DON (from samples filtered in the field through 0.45 μm Fisher syringe filters); and major cations and trace metals (for more see Throckmorton et al., 2015b; Throckmorton et al., 2015a).

2.3 Statistical Analysis

Statistical analyses were performed in R v. 3.614 (R Core Team, 2019) at $\alpha = 0.05$ for analyses of the entire dataset. Analyses for subsets that resulted in limited sample size (*e.g.,* analysis of individual porewater depths or analysis of only the DTLB drainages) were performed at $\alpha = 0.1$, as noted in the text. Pearson correlation analysis was used to assess dependence among DOC variables and other geochemical indicators using the Hmisc package (Harrell Jr, 2019). Depth and sampling month effects were tested using mixed effects models with repeated measures for depth and time using the nlme package

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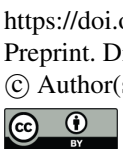

(Pinheiro et al., 2019). When present, interaction effects were investigated using the Phia package (De Rosario-Martinez, 2015). We evaluated the role of site characteristics in driving DOC characteristics using stepwise linear regression with the MASS package (Venables and Ripley, 2002), which evaluates alternate regression models based on AIC criteria. Results are reported as means followed by standard deviations.

3 Results and Discussion

3.1 Temporal and Depth Patterns of DOC Age and Chemistry

DOC $\Delta^{14}C$ values ranged from 19 ‰ to -583 ‰, or from an average conventional radiocarbon age of modern to 7000 y BP, and decreased from July to September ($p < 0.01$, Fig. 2a), consistent with a decline in DOC ^{14}C values from spring through late summer and fall reported for Arctic rivers and their tributaries (Neff et al., 2006; Wild et al., 2019). DOC $\Delta^{14}C$

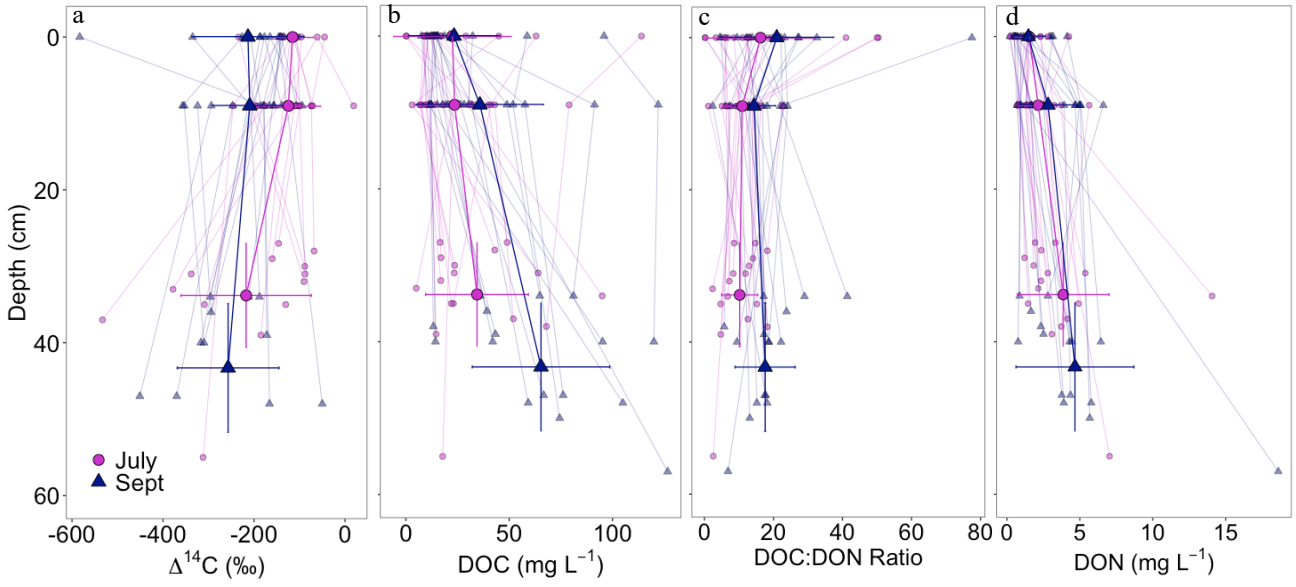

Figure 2. ^{14}C of DOC (a), DOC concentration (b), DOC:DON ratio (c), and DON concentration (d) by depth. Large symbols are means +/- SD. and DON concentration data were presented previously in Throckmorton et al., 2015b.

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185 also declined with depth, consistent with declines in ^{14}C values in soil pore-space CO_2 with depth and from summer to fall in locations in our study area (Vaughn and Torn, 2018). DOC concentrations increased from July to September in samples from the thaw table depth ($p < 0.01$) and increased with depth in September ($p < 0.01$, NS in July, Fig. 2b). DOC concentration and ^{14}C values were not correlated to one another. Interestingly, DOC:DON ratio did not change with depth, but did increase from July to September ($p = 0.01$, Fig. 2c) – an indication that dissolved organic matter (DOM) quality or source may have shifted
190 over the summer. Dissolved organic nitrogen (DON) increased with depth ($p < 0.01$) but did not change between July and September (Fig. 2d). These patterns are consistent with increased mobilization of undecomposed, vegetation-derived C from old permafrost as the thaw table deepened from an average of 34 cm in July to 43 cm in September.

We further assessed the chemistry of DOC with UV-vis absorbance at 254, 350, and 440 nm to identify trends in DOC chemical composition over the sampling period. We targeted these wavelengths because absorption increases with
195 increasing aromaticity at 254 nm (Weishaar et al., 2003), increasing lignin phenol content at 350 nm (Spencer et al., 2008; Mann et al., 2016), and increasing molecular size at 440 nm (Yacobi et al., 2003). We found that absorbances at all 3 wavelengths were positively correlated with DOC and DON concentrations (Figs. S1 and S2). Averaged across depths, the absorbance coefficient at 440 nm increased from 10 m^{-1} in July to 20 m^{-1} in September ($p = 0.03$), consistent with a shift toward a more plant-derived source, but this difference was not significant when weighted by DOC concentration ($SUVA_{440}$, $p = 0.09$,
200 Fig. 3c). $SUVA_{350}$ increased with depth ($p = 0.03$, Fig. 3b), suggesting relatively higher lignin phenols at the thaw table where DOC was produced from actively thawing permafrost. Sampling month and depth effects on $SUVA_{254}$ were not statistically significant. However, correlation analyses suggested $SUVA_{350}$ increased with increasing DON concentration ($\rho = 0.26$, $p = 0.01$) and $SUVA_{254}$ increased with decreasing DOC:DON ratio ($\rho = -0.21$, $p < 0.01$). Surprisingly, across the entire dataset, none of the SUVA indicators were correlated with DOC ^{14}C (Fig. S3).

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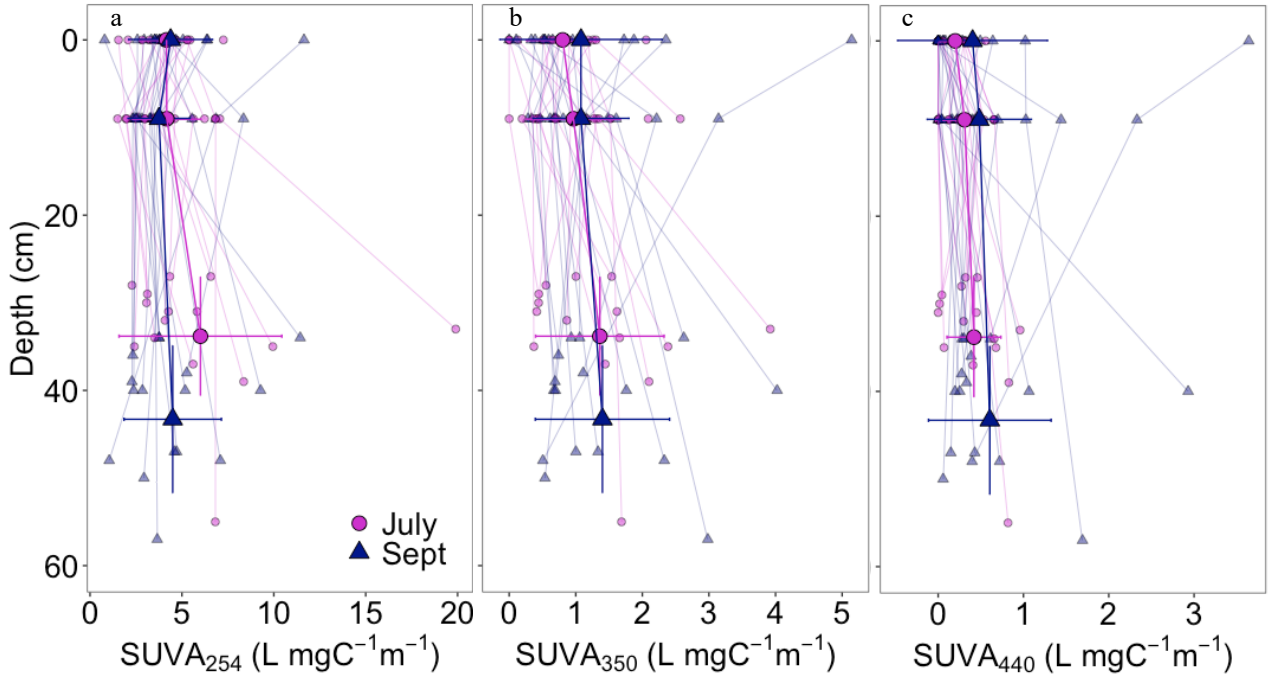

Figure 3. $SUVA_{254}$ (a), $SUVA_{350}$ (b), and $SUVA_{440}$ by depth. Large symbols are means +/- SD.

We observed $SUVA_{254}$ values that are generally higher than those reported for Arctic rivers and streams, which tend to be less than 5 L mg C^{-1} m^{-1} (O'donnell et al., 2012; Spencer et al., 2008; Neff et al., 2006; Drake et al., 2018b), and within the range of those reported for soil leachates from elsewhere in northern Alaska (Gao et al., 2018; Whittinghill et al., 2014). Comparable $SUVA_{350}$ and $SUVA_{440}$ for Arctic terrestrial or aquatic systems are not available in the literature, but in general, the absorption coefficients at these wavelengths observed in this study (Figures S1 and S2) are also higher than those reported for streams and rivers (Spencer et al., 2012; Mann et al., 2016; Spencer et al., 2008). Our observed patterns reflect a DOC source that is high in plant-derived, aromatic, phenolic, and high molecular weight compounds throughout the summer. These trends likely reflect *in situ* production of DOC at depth from thawing permafrost that has not previously undergone microbial processing and may be biolabile.

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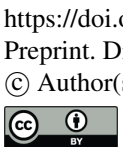

Other biogeochemical indicators (previously published by Throckmorton et al. (2015b)) also changed with sampling depth, consistent with other research on active layer hydrogeochemistry in the area (Newman et al., 2015). Specifically, concentrations of dissolved inorganic carbon (DIC), methane, Fe^{2+}, and Fe^{3+} all increased with depth, while dissolved oxygen (DO) decreased with depth – trends that were attributed to increased availability and use of iron as a terminal electron acceptor in deeper mineral soils (Throckmorton et al., 2015b). Because many of the biogeochemical indicator species changed with depth, the relationship between these variables and DOC characteristics were further assessed separately by sampling depth (surface, shallow, or deep) with an alpha value of 0.1 to account for reduced sample size. In surface and shallow pore waters, DOC $\Delta^{14}C$ values and CH_4 concentrations were positively correlated (surface: $\rho = 0.62$, $n = 17$, $p < 0.01$ and shallow: $\rho = 0.53$, $n = 23$, $p < 0.01$, Fig. 4a), reflecting decreases from July to September in both DOC ^{14}C and CH_4 concentrations ($p = 0.04$).

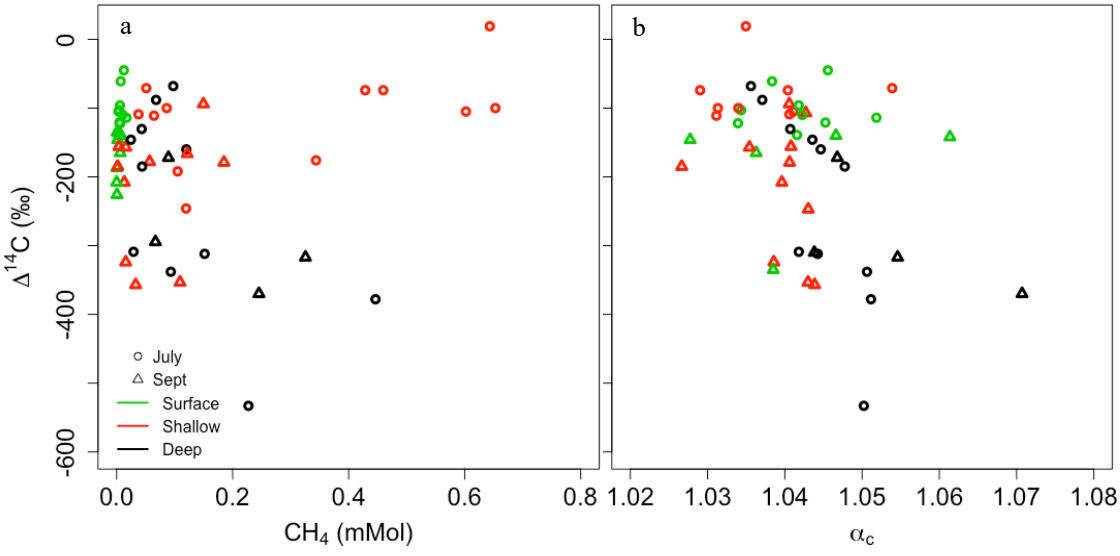

Figure 4. DOC ^{14}C (reported in this study) versus dissolved methane concentration (a) and the apparent fractionation factor for methanogenesis, α_c (b). Methane concentration, $\delta^{13}C$, and α_c data were presented previously in Throckmorton et al., 2015b.

In contrast, deep pore water DOC $\Delta^{14}C$ was negatively correlated with DON ($\rho = -0.38$, $n = 24$, $p = 0.06$), $SUVA_{350}$ ($\rho = -0.39$, $n = 24$, $p = 0.06$), DIC ($\rho = -0.15$, $n = 21$, $p = 0.06$), Fe^{3+} ($\rho = -0.65$, $n = 24$, $p < 0.01$), and dissolved methane ($\rho = -0.59$, $n = 15$, $p = 0.02$, Fig. 4a). None of these variables differed between sampling months, suggesting that these correlations

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reflect differences across sampling sites impacting carbon cycling and redox biogeochemistry. In addition to the trend of older deep porewater DOC with increasing dissolved methane concentrations, deep porewater DOC $\Delta^{14}C$ values were positively correlated with $\delta^{13}C$ of CH_4 ($\rho = 0.45$, $n = 16$, $p = 0.08$) and negatively correlated with the apparent fractionation factor ($\alpha_c = [(\delta^{13}CO_2 + 1000)/(\delta^{13}CH_4 + 1000)]$) for methanogenesis ($\rho = -0.62$, $n = 15$, $p = 0.01$, Fig. 4b). Methane $\delta^{13}C$ values can indicate the dominant pathway for methanogenesis (more depleted values associated with greater hydrogenotrophic methanogenesis and less depleted values associated with greater acetoclastic methanogenesis), but are also affected by other processes including diffusion and methanotrophy (Chanton, 2005). Thus, α_c-values, which represent the difference in stable C isotopic values of both DIC and CH_4, are used to detect shifts in methanogenic pathways, with higher α_c-values indicative of hydrogenotrophic and lower α_c-values typical of acetoclastic methanogenesis (Whiticar et al., 1986; Wilson et al., 2016; Hines et al., 2008). α_c-values also increased with depth ($p < 0.01$) and from July to September in deep porewaters only ($p < 0.01$). The correlation between α_c-values and DOC ^{14}C values is likely not a causal relationship, but rather points to a tendency towards increased hydrogenotrophic relative to acetoclastic methanogenesis in deeper porewaters later in the summer when DOC:DON ratios were also higher.

Our study coincided with work by others on carbon cycling in our study area. Throckmorton et al., 2015 found that acetoclastic methanogensis was the dominant pathway for methane production at all 17 of our sampling locations in July, but that by September four drainages had become predominantly hydrogenotrophic (sites 3, 9, 10, and 15). Unfortunately, out of these 4 sites we only have DOC ^{14}C for deep porewater in September for plot 10, but this sample has the oldest DOC age ($^{14}C = -370$ ‰) of the September samples with a measured $\delta^{13}C$ of CH_4 (-78.7 ‰). Vaughn et al. (2016) measured CO_2 and CH_4 fluxes at sites across a permafrost degradation gradient within some of our study drainages. They found that more degraded sites had lower net CH_4 emissions, higher CH_4 oxidation, and methanogenesis dominated by the hydrogenotrophic pathway (Vaughn et al., 2016).

3.2 Spatial Patterns of DOC Age and Chemistry

Correlation analyses also suggested that DOC characteristics differed with sampling location features. DOC concentration decreased with increasing drainage size ($\rho = -0.22$, $p < 0.01$, Fig. 5a), which ranged from 0.8 to 171 ha. Stepwise

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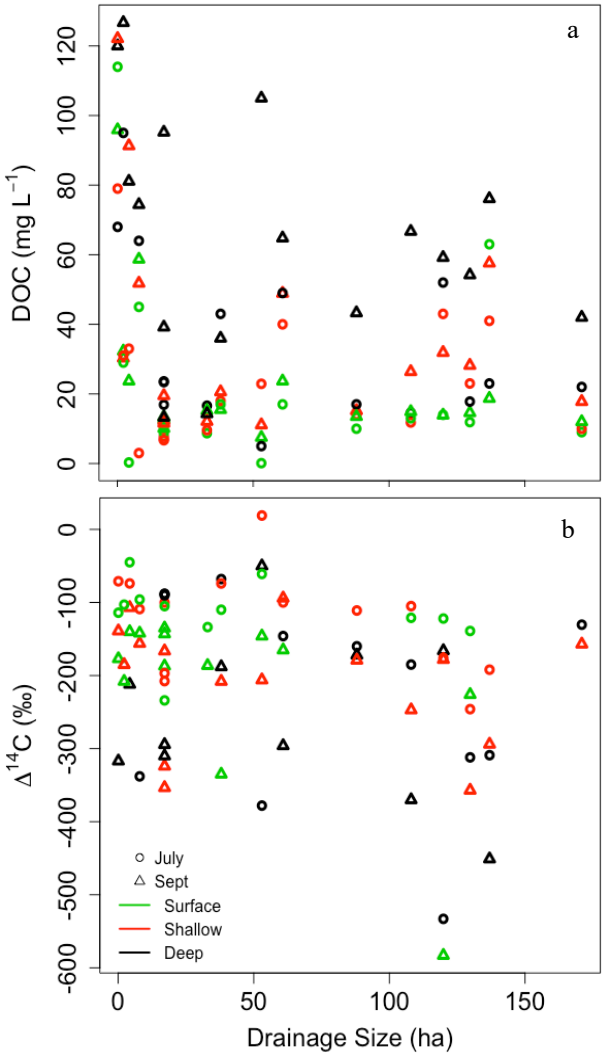

Figure 5. DOC concentration (a) and DOC ^{14}C (b) versus drainage size.

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linear regression indicated including drainage size improved model fit compared to depth and month alone. DOC ^{14}C decreased with increasing drainage size ($\rho = -0.31$, $p < 0.01$). DOC ^{14}C was also correlated to water flow (stagnant or gentle flow observed upon sampling, $\rho = 0.28$, $p = 0.01$). Drainage size and water flow (stagnant or gentle flow) were correlated to one another ($\rho = -0.84$, $p < 0.01$), such that wetland drainages with more stagnant waters tended to be smaller than channel drainages with

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gentle lateral flow, so stepwise linear regression was used to identify that the best model for predicting DOC ^{14}C values included sampling month, depth, and drainage size. Controlling for month and depth, DOC ^{14}C values decreased with increasing drainage size ($p = 0.01$, Fig. 5b), likely reflecting greater production of relatively young DOC within the smaller drainages because these streams are not as deeply incised as the larger basins, and thus tap into a younger permafrost carbon reservoir. Others have reported that small headwater streams and catchments had higher DOC ^{14}C values (Neff et al., 2006), higher $SUVA_{254}$ (Coch et al., 2019), and larger fractions of biodegradable DOC (Vonk et al., 2015a) than large rivers, while decreasing DOC with increasing size of thaw lakes has been observed in areas of Western Siberia undergoing permafrost thaw (Shirokova et al., 2013).

In the drained thaw lake basins (DTLBs), depth to the thaw table in young (< 50 years) and medium (50–300 years) aged DTLB's was shallower by 10 cm on average than in old (300–2000 years) and ancient (2000–5500 years) DTLBs ($p < 0.01$). In deep pore waters, DOC concentrations decreased with increasing basin age ($p = 0.03$, Fig. 6a) controlling for depth and month. Also in deep pore waters, correlation analyses indicated that $SUVA_{350}$ ($\rho = -0.54$, $n = 16$, $p = 0.03$, Fig. 6b) and $SUVA_{440}$ ($\rho = -0.66$, $n = 16$, $p < 0.01$, Fig. 6c) decreased with increasing basin age, suggesting a decrease in lignin phenols and high molecular weight compounds associated with fresh vegetation-derived organic matter as DTLBs age. Our interpretation is limited, as we only sampled from 8 DTLBs, only one of which was younger than 50 years. However, these trends may reflect a decline in readily decomposable carbon and increase in the degree of organic matter decomposition as DTLB's age as reported across 77 basins on the Barrow Peninsula (Hinkel et al., 2003) and in Western Siberia thaw lakes, where DOC concentrations and high molecular weight compounds declined across a chronosequence of lake development (Pokrovsky et al., 2011).

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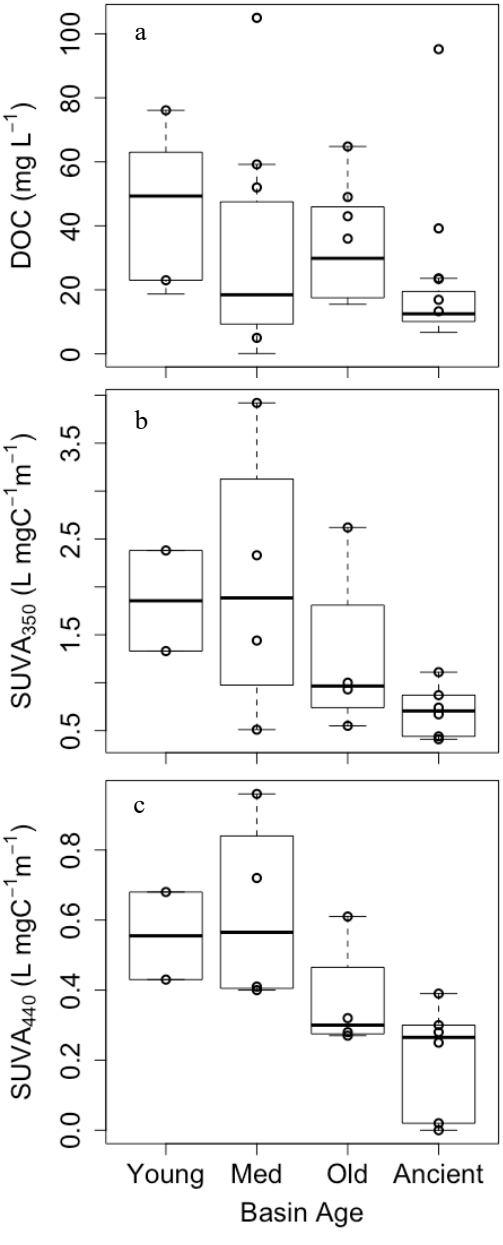

Figure 6. DOC concentration across depths (a), $SUVA_{350}$ in deep pore waters (b), and $SUVA_{440}$ in deep pore waters (c) versus DTLB age (young: < 50 years; medium: 50–300 years; old: 300–2000 years; and ancient 2000–5500 years).

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4 Summary and Conclusions

By studying 17 drainages in and around the Barrow Experimental Observatory, we found that DOC age and concentration in surface, shallow pore, and deep pore waters increased with depth and as the thaw table deepened from July to September. We observed small shifts in DOC chemistry over the summer, including an increase in DOC:DON ratios and α_{440}, the absorption coefficient that correlates with high molecular weight organic matter. Indicators of DOC chemistry reflected a DOC source consistent with unprocessed organic matter throughout the summer: high in aromaticity, lignin phenols, and high molecular weight compounds. Smaller wetland drainages released younger DOC that was higher in aromatics relative to larger drainage channels, while younger DTLBs released younger DOC that was higher in lignin phenols and high molecular weight compounds than older DTLBs. Across our study area, we found that older DOC and younger DOC have similar chemical indicators of lability, suggesting that the production of old and labile DOC may continue with increased permafrost thaw as the active layer deepens and thaw seasons lengthen in the northern Arctic.

Data availability

New data associated with this manuscript have been added to Throckmorton et al., 2015a. All data are available here: https://ngee-arctic.ornl.gov/data/pages/NGA027.html

Supplement

Author Contribution

KJM, HMT, JMH, BDN, and CJW designed the research. KJM, TPG, and CJW secured funding. HMT, JMH, BDN, and CJW performed fieldwork. KJM, ALH, and HMT performed laboratory analyses. KJM performed data analysis. All authors contributed to interpretation. KJM wrote manuscript with input from all authors.

Competing interests

The authors declare that they have no conflict of interest.

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