

Source water controls on the character and origin of dissolved organic matter in streams of the Yukon River basin, Alaska

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[1] Climate warming and permafrost degradation at high latitudes will likely impact watershed hydrology, and consequently, alter the concentration and character of dissolved organic carbon (DOC) in northern rivers. We examined seasonal variation of DOC chemistry in 16 streams of the Yukon River basin, Alaska. Our primary objective was to evaluate the relationship between source water (shallow versus deep groundwater flow paths) and DOC chemical composition. Using base cation chemistry and principal component analysis, we observed high contributions of deep groundwater to glacial and clearwater streams, whereas blackwater streams received larger contributions from shallow groundwater sources. DOC concentration and specific ultraviolet absorbance peaked during spring snowmelt in all streams, and were consistently higher in blackwater streams than in glacial and clearwater streams. The hydrophobic acid fraction of DOC dominated across all streams and seasons, comprising between 35% and 56% of total DOC. The hydrophilic acid fraction of DOC was more prominent in glacial ($23\% \pm 3\%$) and clearwater streams ($19\% \pm 1\%$) than in blackwater streams ($16\% \pm 1\%$), and was enriched during winter base flow ($29\% \pm 1\%$) relative to snowmelt and summer base flow. We observed that an increase in the contribution of deep groundwater to streamflow resulted in decreased DOC concentration, aromaticity, and DOC-to-dissolved organic nitrogen ratio, and an increase in the proportion of hydrophilic acids relative to hydrophobic acids. Our findings suggest that future permafrost degradation and higher contributions of groundwater to streamflow may result in a higher fraction of labile DOM in streams of the Yukon basin.

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1. Introduction

[2] The boreal forest contains approximately one third of the world's terrestrial organic carbon (C) [Post *et al.*, 1982; Dixon *et al.*, 1994; McGuire *et al.*, 2002]. Recent warming at high latitudes will likely accelerate rates of C cycling directly by increasing rates of biological processes (e.g., net primary production, decomposition) and indirectly via ecosystem disturbances (e.g., wildfire, permafrost thaw) [Goulden *et al.*, 1998; Zhuang *et al.*, 2004; Davidson and Janssens, 2006]. Warming at high latitudes may also modify the transfer of dissolved organic carbon (DOC) from terrestrial to aquatic and marine ecosystems [Frey and Smith, 2005; Striegl *et al.*,

2005]. DOC fluxes are generally higher in streams draining boreal forest catchments than in temperate or tropical biomes [Hope *et al.*, 1994; Aitkenhead and McDowell, 2000; Neff and Asner, 2001], and can be an important component of ecosystem C balance [Waddington and Roulet, 1997; Roulet *et al.*, 2007]. Furthermore, microbial mineralization of DOC in aquatic habitats is an important source of carbon dioxide to the atmosphere [Kling *et al.*, 1991].

[3] The concentration and chemical composition of dissolved organic matter (DOM) in streams varies seasonally and is strongly influenced by discharge [Boyer *et al.*, 1997; Hornberger *et al.*, 1994; Laudon *et al.*, 2004; Petrone *et al.*, 2006]. At high latitudes, more than 55% of the annual DOC flux occurs during spring snowmelt [Finlay *et al.*, 2006], which dominates annual hydrographs in the boreal region [Slaughter and Kane, 1979; Carey and Woo, 1998]. During snowmelt, overland flow, and routing of meltwater through shallow litter and organic soils results in the transfer of large quantities of DOC from terrestrial to aquatic ecosystems. Following snowmelt, thawing of near-surface soils governs the depth of lateral flows and, consequently, influences DOC concentrations and character during summer base flow [Carey, 2003; Neff *et al.*, 2006]. During winter, refreezing of

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Table 1. Study Stream Types and Locations

Watershed	Stream Type	Latitude, °N; Longitude, °W (NAD 83) ^a	Site Number (Figure 1)
Parks Stream	Blackwater	64°46'28.7", 148°16'81.6"	1
Washington Creek	Blackwater	65°09'03.1", 147°51'23.6"	2
Tatalina River	Blackwater	65°19'45.4", 148°18'28.2"	3
Tolovana River	Blackwater	65°28'16.9", 148°16'01.7"	4
Hess Creek	Blackwater	65°39'55.6", 149°05'44.6"	5
Fort Hamlin Hills	Blackwater	66°01'97.0", 150°07'68.8"	6
No Name Creek	Blackwater	66°07'00.9", 150°09'78.6"	7
Fish Creek	Blackwater	66°32'32.4", 150°47'49.7"	8
Dalton Central	Blackwater	66°36'67.8", 150°41'30.1"	9
Prospect Creek	Blackwater	66°46'92.8", 150°41'14.4"	10
Jim River	Blackwater	66°53'08.5", 150°31'32.7"	11
Middle Fork, Koyukuk River	Glacial	67°26'25.8", 150°04'53.9"	12
Gold Creek	Clearwater	67°30'77.2", 149°50'97.8"	13
Dietrich River	Glacial	67°37'74.4", 149°44'28.0"	14
Cobble Creek	Clearwater	67°47'56.9", 149°45'10.3"	15
Dalton North	Clearwater	67°47'56.9", 149°48'12.4"	16

^aNAD 83, North American Datum of 1983.

the active layer limits hydrologic inputs from the catchment and many streams completely freeze. However, discharge in some streams persists throughout the winter, due to groundwater inputs from deeper source waters. Streams receiving groundwater from these sources typically have low DOC concentrations ($<2 \text{ mgC L}^{-1}$) [Striegl *et al.*, 2007], and, in some instances, groundwater can be an important source of DOC to streams [Ford and Naiman, 1989].

[4] In the boreal region, the presence or absence of permafrost also functions as an important control on DOC concentration in streams [MacLean *et al.*, 1999; Carey, 2003; Petrone *et al.*, 2006]. Permafrost influences watershed hydrology by restricting infiltration of shallow soil water into mineral soil, which reduces soil drainage and confines groundwater flow to shallow organic horizons. As a result, streams in permafrost-dominated watersheds tend to have higher DOC but lower dissolved mineral concentrations (such as calcium and magnesium) than watersheds that are mostly permafrost-free [MacLean *et al.*, 1999; Carey, 2003; Petrone *et al.*, 2006]. Discontinuous permafrost in interior Alaska is warming and thawing [Osterkamp and Romanovsky, 1999; Jorgenson *et al.*, 2001], which may alter watershed hydrology and C export in streamflow. Several studies have hypothesized that permafrost thaw will reroute subsurface flow through deeper mineral soils, reducing DOC inputs to northern rivers [MacLean *et al.*, 1999; Striegl *et al.*, 2005]. For instance, data presented in Walvoord and Striegl [2007] suggest that the amount of groundwater contributing to stream discharge has increased in recent decades in the Yukon River basin, Alaska, presumably in response to permafrost thaw in the basin.

[5] The chemical composition of DOC in streams is linked to organic matter sources, soil microbial processes, and the hydrology of the stream watershed [McKnight *et al.*, 1997; Hood *et al.*, 2003, 2005]. In interior Alaska, pore water DOC at the organic/mineral soil interface in black spruce ecosystems is typically dominated by aromatic hydrophobic acids, and tends to decompose very slowly [Wickland *et al.*, 2007]. During snowmelt, the chemical composition of stream DOC closely reflects the terrestrially derived organic matter from surface organic horizons [Striegl *et al.*, 2005, 2007], as overland and near-surface groundwater flow are the dominant sources contributing to streamflow [Carey, 2003].

During winter base flow, when streamflow is dominated by groundwater inputs, DOC is generally less aromatic and composed of fewer hydrophobic compounds [Striegl *et al.*, 2005, 2007], reflecting more microbial processing of C compounds and longer hydraulic residence times [McKnight and Aiken, 1998].

[6] Most research on DOC in the Yukon River basin has focused on large high-order rivers [Guo and Macdonald, 2006; Striegl *et al.*, 2005, 2007], small headwater streams [MacLean *et al.*, 1999; O'Donnell and Jones, 2006; Petrone *et al.*, 2006, 2007; Balcarczyk *et al.*, 2009], or soils [Kane *et al.*, 2006; Wickland *et al.*, 2007]. However, streams of the Yukon River basin drain watersheds with varying permafrost extent [Brown and Péwé, 1973], fire history [Murphy *et al.*, 2000], and hydrology [MacLean *et al.*, 1999; Petrone *et al.*, 2006]. Herein, we examine seasonal changes in DOC chemistry in 16 streams varying in source water inputs along a latitudinal gradient between Fairbanks in the south and the Brooks Range to the north. Our primary research objectives were to evaluate (1) the contribution of different source waters (shallow versus deep groundwater) to streamflow, (2) the seasonal variation in the concentration and chemical character of stream DOM, and (3) the relationship between source water and DOM chemical composition. From these findings, we will examine the implications of future permafrost thaw within the Yukon River basin on the chemical composition and reactivity of DOM.

2. Methods

2.1. Study Sites and Experimental Design

[7] We sampled 16 interior Alaskan streams draining small sub-catchments of the Yukon River basin along a latitudinal gradient between Fairbanks and the Brooks Range, spanning a range of nearly 500 km (Table 1 and Figure 1). The Yukon basin covers 853,300 km² of northwest Canada and Alaska, and primarily consists of remote wilderness. Precipitation in interior Alaska is relatively low, averaging 250–550 mm yr⁻¹. Much of the Yukon basin is underlain by permafrost, which is actively warming and thawing throughout the basin [Osterkamp and Romanovsky, 1999; Jorgenson *et al.*, 2001]. Upland vegetation in Yukon basin sub-catchments is dominated by black spruce (*Picea mariana*), white spruce (*Picea*

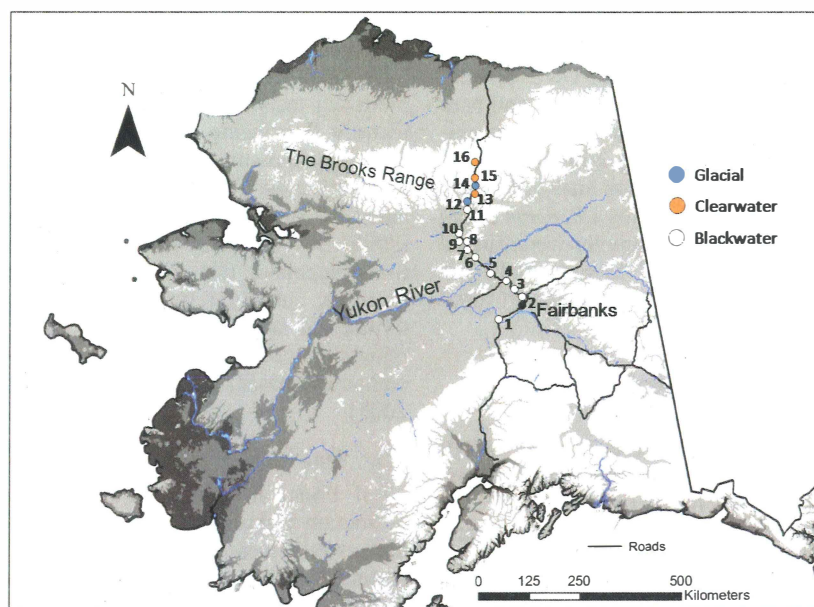


Figure 1. Map of site locations along Elliot and Dalton Highways between Fairbanks and the Brooks Range, Alaska. Numbers represent stream identifiers as listed in Table 1.

glauca), quaking aspen (*Populus tremuloides*), and paper birch (*Betula papyrifera*). Valley bottoms are typically poorly drained and vegetation cover often consists of black spruce, shrubs, and moss hummocks. Approximately 30% of the Yukon basin is covered by low-lying wetlands.

[8] We sampled streams and rivers that varied with respect to the origin of waters contributing to streamflow. In glacially fed streams (Middle Fork of the Koyukuk River and Dietrich River), flow originates as meltwater from perennial ice and snow fields and alpine glaciers. Melting of glacial ice has been shown to increase stream discharge in southeast Alaska [Neal *et al.*, 2002]. During the summer, these streams typically have high sediment loads of unweathered glacial flour, low DOC concentrations, and high dissolved inorganic carbon (DIC) concentrations [Striegl *et al.*, 2007]. In clearwater streams (Cobble Creek, Gold Creek, and Dalton North Creek), flow is dominated by groundwater inputs, and stream chemistry is characterized by low DOC concentrations, low sediment concentrations, and high DIC concentrations [Striegl *et al.*, 2007]. The clearwater streams sampled in this study are relatively small headwater streams that ultimately flow into the larger Middle Fork of the Koyukuk River. Blackwater streams ($n = 12$ along the latitudinal gradient) receive water from riparian wetlands and runoff perched by seasonal ice and permafrost. Subsurface flow in these systems is, therefore, confined to shallow soil horizons in the active layer above the permafrost table [MacLean *et al.*, 1999; Carey, 2003]. As a result of these hydrologic conditions, blackwater streams typically have high DOC and low DIC concentrations [Striegl *et al.*, 2007].

[9] Few data are available with respect to the hydrology and watershed characteristics of the streams surveyed here, with some exceptions [e.g., Dornblaser and Halm, 2006]. Hess Creek, a representative blackwater stream underlain by discontinuous permafrost, originates in the hills south of the

Yukon Flats National Wildlife Refuge, and flows west where it intersects the Dalton Highway and then eventually joins the main stem of the Yukon River. The USGS has some historical streamflow data for Hess Creek from 1970–1978, during which peak discharge averaged $150 \text{ m}^3 \text{ s}^{-1}$ [Dornblaser and Halm, 2006]. The Koyukuk River originates in the Endicott and Philip Smith Mountains of the Brooks Range, and flows south through the Kanuti and Koyukuk national wildlife refuges, where it ultimately enters the main stem of the Yukon River. The Middle Fork of the Koyukuk is located in the Brooks Range, far from the Koyukuk's confluence with the Yukon River, and drains an area underlain by continuous permafrost. Most watersheds in the Yukon River basin have a rich and complex fire history, but little data are available with respect to site-specific fire characteristics (e.g., fire return interval, burn severity). The watershed of No Name Creek, a mid-order blackwater stream, burned near our sampling point along the Dalton Highway during the summer of 2004.

[10] Streams were sampled monthly from June through September 2005 and once in April, May, and July of 2006. Samples obtained in April reflected “winter base flow” hydrologic conditions. In many cases, streams were frozen from the stream surface to the sediment bottom, indicating minimal inputs from deep groundwater to streamflow. In other streams, we observed flowing water under a thick layer of ice, suggesting a significant contribution of deep groundwater to streamflow. Spring snowmelt samples were collected in May 2006, and reflect the melting of snowpack routed through surface soil horizons (i.e., shallow groundwater [Carey, 2003]). The remaining samples were obtained during summer base flow conditions between the months of June and September, and likely reflect mixing of shallow and deep groundwater sources. While we did not directly measure source water chemistry, prior investigations have shown that calcium and magnesium concentrations are generally higher

in deep groundwater than in shallow groundwater [Hinzman *et al.*, 2006].

[11] All stream samples were analyzed for DOC concentration, specific ultraviolet absorbance (SUVA_{254}), and base cation concentrations (Ca^{2+} , Mg^{2+} , K^+ , Na^+). Samples collected from September 2005 through July 2006 were additionally characterized by DOC fractionation analyses [Aiken *et al.*, 1992] and fluorescence spectroscopy [Stedmon *et al.*, 2003; Cory and McKnight, 2005]. All samples were filtered within 4–6 hours of sampling using a Gelman 0.45 μm membrane filter (rinsed with sample) and stored at 4°C until analysis.

2.2. DOC, UV-Vis, and dissolved organic nitrogen (DON)

[12] DOC concentrations were determined using an OI Analytical Model 700 TOC Analyzer via platinum-catalyzed persulfate wet oxidation method [Aiken *et al.*, 1992]. UV-Vis absorbance was measured at room temperature using a quartz cell with a path length of 1 cm on a Hewlett-Packard Model 8453 photodiode array spectrophotometer. UV absorption data are reported at $\lambda = 254 \text{ nm}$. SUVA_{254} was determined by dividing the UV-Vis absorbance at $\lambda = 254 \text{ nm}$ by DOC concentration. SUVA_{254} , which is typically used as a measure of DOC aromaticity, provides an “average” molar absorptivity at 254 nm for the DOC [Weishaar *et al.*, 2003]. SUVA_{254} is reported in units of $\text{L mgC}^{-1} \text{ m}^{-1}$. Cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+) and anions (NO_2^- , NO_3^-) were analyzed on a Dionex DX-320 Ion Chromatograph (Dionex Corporation, Sunnyvale, CA, USA). Total dissolved nitrogen was determined using a Shimadzu TNM-1 total nitrogen measuring unit. DON was calculated as the difference between total dissolved nitrogen and dissolved inorganic nitrogen (NO_2^- , NO_3^- , NH_4^+).

2.3. DOM Fractionation

[13] Stream water samples were chromatographically separated into four different fractions: hydrophobic acids, hydrophobic neutrals, hydrophilic organic matter, and transphilic acids using Amberlite XAD-8 and XAD-4 resins [Aiken *et al.*, 1992]. The resins preferentially sorb different classes of organic acids based on aqueous solubility of the solute, chemical composition of the resin, resin surface area, and resin pore size. The amount of organic matter within each fraction, expressed as a percentage of the total DOC concentration, was calculated using the DOC concentration and the sample mass of each fraction. UV-Vis absorption was run on each of the major DOC fractions. The standard deviation for the mass percentages of the fractionation was $\pm 2\%$.

2.4. DOM Fluorescence

[14] Fluorescence excitation-emission matrices (EEMs) were measured on select samples at room temperature using a Jobin-Yvon Horiba Fluoromax-3 fluorometer. Samples were diluted with deionized water when necessary, to a UV absorbance at $\lambda = 254 \text{ nm}$ of 0.4 absorbance units (1 cm cell). EEMs were collected over an excitation range of 240–450 nm every 5 nm, and an emission range of 300–600 nm every 2 nm. Scans were blank-subtracted, Raman-normalized, and corrected for inner-filter effects [McKnight *et al.*, 2001]. Fluorescence index (FI) was determined as the ratio of the

intensities at excitation (ex) and emission (em) wavelengths ex370/em470 and ex370/em520.

[15] Parallel factor analysis (PARAFAC), a statistical modeling technique, was applied to fluorescence EEMs to identify fluorescing components according to their unique excitation and emission patterns [Stedmon *et al.*, 2003; Cory and McKnight, 2005]. EEMs were fit to the previously validated 13-component model presented in Cory and McKnight [2005]. Seven of these components are identified as quinone-like compounds (Q1-Q3, SQ1-SQ3, and HQ), which vary in redox state and degree of conjugation. Tyrosine and tryptophan are identified as protein-like fluorophores; the remaining components are not associated with a particular compound class [McKnight *et al.*, 2001; Cory and McKnight, 2005].

2.5. Statistical Analyses

[16] Principal component analysis (PCA) was used as an ordination technique to examine variation in source water chemistry across study streams (PROC PRINCOMP; SAS Institute). This ordination procedure was used to both infer the chemistry of source waters and also confirm our a priori classification of stream types (blackwater, clearwater, or glacial streams; Table 1) based on an understanding of local geography and field observation. Seasonal variation in stream DOC concentration and SUVA_{254} were analyzed using a mixed effects analysis of variance (analysis of variance (ANOVA); PROC MIXED; SAS Institute), with stream type and date as fixed effects, and stream identifier as a random effect to account for repeated measures. The model included all interactions between fixed main effects, and accounted for any unbalanced data. Linear regression techniques were used (PROC REG; SAS Institute) to analyze the relationship between FI and SUVA_{254} , and to evaluate the relationship between source water and DOC concentration and chemical character. DOC concentrations, SUVA_{254} values, and DOM chemical fractions are reported as means $\pm$ one standard error. Means were calculated from replicate stream samples collected for a given stream type (blackwater, clearwater, or glacial streams) during a given hydrologic condition (winter base flow, spring snowmelt, summer base flow). Mean DOC concentration and SUVA_{254} values are reported to demonstrate the large seasonal differences typical of these systems, as well as general behavioral differences among streams.

3. Results

3.1. Cations, Anions, and Source Water Contributions to Study Streams

[17] Base cation concentrations were highly variable across study streams receiving inputs from different source waters (Table 2). Stream sodium concentration averaged $2.67 \pm 0.73 \text{ mg L}^{-1}$ across the 16 streams, with values ranging from $5.36 \pm 0.61 \text{ mg L}^{-1}$ in the Dietrich River (glacial) to $1.12 \pm 0.09 \text{ mg L}^{-1}$ in the Jim River (blackwater). Magnesium concentration averaged $9.91 \pm 2.80 \text{ mg L}^{-1}$ across the 16 streams, and ranged from $1.5 \pm 0.4 \text{ mg L}^{-1}$ in Fish Creek (blackwater) to $36.5 \pm 11.7 \text{ mg L}^{-1}$ in Cobble Creek (clearwater). Potassium concentration averaged $0.29 \pm 0.10 \text{ mg L}^{-1}$ across the 16 streams, and ranged from $0.03 \pm 0.01 \text{ mg L}^{-1}$ in Cobble Creek (clearwater) to $0.64 \pm 0.40 \text{ mg L}^{-1}$ in the Parks Stream (blackwater stream). Calcium concentration aver-

Table 2. Mean Base Cation Concentrations for Study Streams

Watershed	Number of Samples	Na (mg L ⁻¹)	Mg (mg L ⁻¹)	K (mg L ⁻¹)	Ca (mg L ⁻¹)
Cobble Creek	6	1.94 ± 0.27	36.5 ± 11.7	0.03 ± 0.01	91.3 ± 30.2
Dalton Central	7	1.54 ± 0.44	1.8 ± 0.5	0.22 ± 0.08	5.2 ± 1.3
Dalton North	5	3.89 ± 2.40	7.6 ± 4.6	0.09 ± 0.07	43.8 ± 42.3
Dietrich River	6	5.36 ± 0.61	23.1 ± 5.3	0.08 ± 0.03	49.0 ± 12.1
Fish Creek	6	1.65 ± 0.16	1.5 ± 0.4	0.30 ± 0.02	4.7 ± 0.8
Fort Hamlin Hills	6	3.74 ± 1.09	3.1 ± 0.7	0.26 ± 0.04	16.8 ± 4.0
Gold Creek	4	3.31 ± 1.03	24.9 ± 9.8	0.12 ± 0.08	46.4 ± 15.6
Hess Creek	5	1.62 ± 0.24	6.8 ± 1.1	0.39 ± 0.14	22.4 ± 3.6
Jim River	4	1.12 ± 0.09	2.3 ± 0.4	0.27 ± 0.03	10.4 ± 1.8
Middle Fork, Koyukuk River	7	4.10 ± 1.20	18.2 ± 5.1	0.11 ± 0.03	43.5 ± 12.3
No Name Creek	7	4.81 ± 2.04	3.9 ± 0.3	0.50 ± 0.10	22.7 ± 1.2
Prospect Creek	3	1.17 ± 0.20	3.6 ± 0.6	0.36 ± 0.08	19.8 ± 3.7
Tatalina River	4	1.18 ± 0.16	3.6 ± 0.4	0.22 ± 0.02	7.3 ± 0.7
Tolovana River	4	1.95 ± 0.45	6.3 ± 1.3	0.63 ± 0.38	15.1 ± 2.8
Washington Creek	6	3.19 ± 0.81	7.8 ± 1.1	0.33 ± 0.06	13.8 ± 1.8
Parks Stream	7	2.14 ± 0.57	7.6 ± 1.6	0.64 ± 0.40	17.1 ± 3.5

aged 26.8 ± 8.6 mg L⁻¹ across the 16 streams, and ranged from 4.7 ± 0.8 mg L⁻¹ in Fish Creek (blackwater) to 91.3 ± 30.2 mg L⁻¹ in Cobble Creek (clearwater). Nitrate concentration varied with stream type, averaging 0.35 ± 0.05 , 0.59 ± 0.09 , and 1.00 ± 0.22 mg L⁻¹ in blackwater, glacial, and clearwater streams, respectively. Ammonium concentrations were generally low and did not vary substantially across study streams, averaging 0.03 ± 0.01 mg L⁻¹, collectively.

[18] Source water contributions to streamflow, as indicated by base cation chemistry, varied among stream types (Figure 2). The first two principal components collectively explained 77% of the variance in base cation chemistry. Principal component (PC) axis 1 was positively correlated with stream calcium and magnesium concentration, and negatively correlated with potassium concentration. PC axis 2 was most strongly correlated with sodium concentration. By plotting the first two principal components against each other, we were able to interpret differences in source water contribution to surface flow across stream types. PC axis 1 separated streams receiving water from groundwater or meltwater sources (clearwater, glacial) and streams receiving inputs from shallow groundwater flowing through the soil active layer (blackwater streams). Clearwater and glacial streams clustered relatively tightly, whereas blackwater streams formed a broader band across PC axis 2.

3.2. Seasonal Patterns in DOC Concentration and SUVA₂₅₄

[19] DOC concentration varied with stream type (mixed-effects ANOVA; $df = 2$, $F = 7.89$, $P = 0.0007$) and sample dates ($df = 6$, $F = 2.26$, $P = 0.046$). In general, stream DOC concentration peaked during spring snowmelt, was lowest during winter base flow, and intermediate in value during summer base flow (Figure 3a and Table 3). In blackwater streams, DOC concentration increased from 4.3 ± 1.3 mgC L⁻¹ during winter base flow to 29.4 ± 2.6 mgC L⁻¹ during spring snowmelt. During summer base flow, DOC concentrations in blackwater streams ranged from 11.1 to 22.3 mgC L⁻¹. In the Middle Fork of the Koyukuk River, a glacially fed stream, DOC increased from 1.1 mgC L⁻¹ during winter base flow to 10.3 mgC L⁻¹ during spring snowmelt, and ranged from 1.7 to 3.6 mgC L⁻¹ during summer base flow. DOC concentration in Dalton North Creek, a clearwater stream, increased from 3.6 to 8.2 mgC L⁻¹ between winter base flow and spring snow-

melt, and ranged from 0.8 to 10.8 mgC L⁻¹ during summer base flow.

[20] Stream SUVA₂₅₄ values varied with stream type ($df = 2$, $F = 25.27$, $P < 0.0001$) and across sample dates ($df = 6$, $F = 5.20$, $P = 0.0002$). SUVA₂₅₄ was generally lower during winter base flow than during spring snowmelt and summer base flow (Figure 3b and Table 3). In blackwater streams, SUVA₂₅₄ peaked during spring snowmelt, averaging 3.9 ± 0.04 L mgC⁻¹ m⁻¹, and was lowest during winter base flow, averaging 2.8 ± 0.1 L mgC⁻¹ m⁻¹. During summer base flow, SUVA₂₅₄ values ranged from 2.6 to 3.4 L mgC⁻¹ m⁻¹ in blackwater streams. In the Middle Fork of the Koyukuk River, a glacially fed river, SUVA₂₅₄ values also peaked during spring snowmelt at

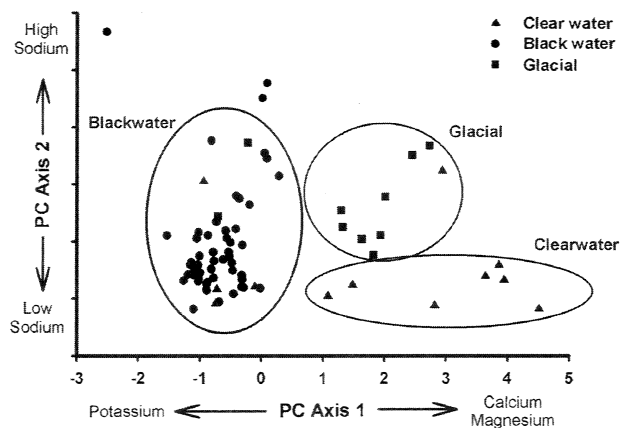


Figure 2. Results of principal component analysis (PCA) to evaluate differences in source waters contributing to surface flow in study streams. Each point represents a stream sample collected during summer base flow conditions. The first and second principal components (PCs) explained 53% and 24% of the variation in base cation chemistry, respectively. PC axis 1 was positively correlated with Ca and Mg concentration and was negatively correlated with K concentration. PC axis 2 was positively correlated with Na concentration. Ovals drawn around the blackwater (circles), glacial (squares), and clearwater (triangles) samples are for illustrative purposes only.

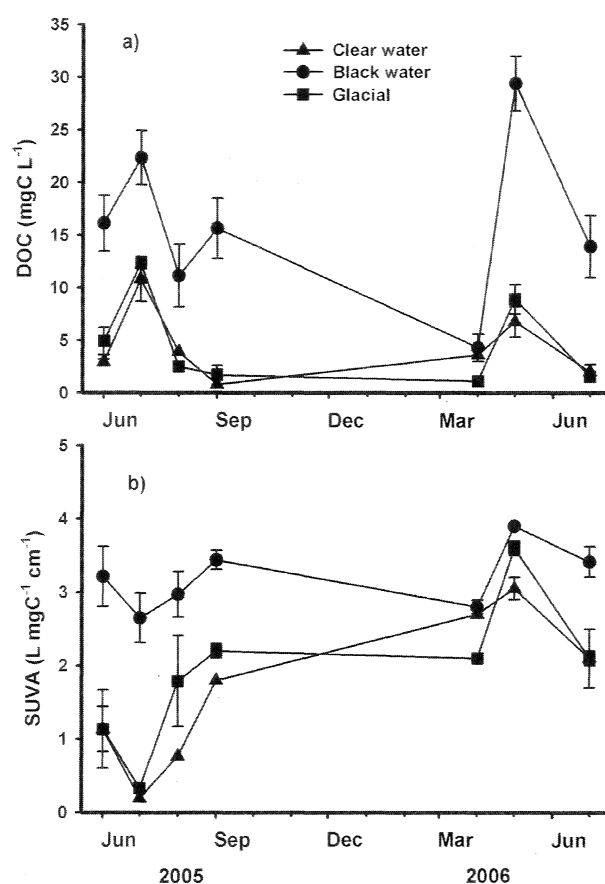


Figure 3. Temporal variation in stream (a) dissolved organic carbon (DOC) concentration and (b) specific ultraviolet absorbance (SUVA₂₅₄) across three stream types (clearwater, blackwater, glacial). Each point represents the mean value for all streams on a given date.

3.7 L mgC⁻¹ m⁻¹, but were not different between winter and summer base flow, averaging 2.0 ± 0.3 L mgC⁻¹ m⁻¹. In Dalton North Creek, a clearwater stream, SUVA₂₅₄ values peaked during spring snowmelt at 3.2 L mgC⁻¹ m⁻¹, and did not differ between winter and summer base flow, averaging 2.3 ± 0.3 L mgC⁻¹ m⁻¹.

3.3. Seasonal Variation in DOC Chemical Fractions

[21] The hydrophobic acid fraction was the dominant fraction of the DOC in all stream samples; however, the relative proportion of hydrophobic acids varied across stream types and seasons (Figure 4). In general, blackwater streams had a higher proportion of hydrophobic acids, averaging $56\% \pm 1\%$ and $53\% \pm 1\%$ in spring and summer, respectively. The hydrophilic fraction in blackwater streams averaged $17\% \pm 1\%$ in spring and $15\% \pm 1\%$ in summer, and accounted for a lower proportion of DOC than in glacially fed (spring and summer average = $23\% \pm 3\%$) or clearwater streams (spring and summer average = $19\% \pm 1\%$).

[22] DOC concentrations during winter base flow were generally too low to conduct the DOC fractionation analyses, except for No Name Creek and Washington Creek (Table 4). In these two blackwater streams, the hydrophobic acid fraction was also the dominant organic matter fraction across all seasons. However, the proportion of hydrophobic acids was substantially lower during winter base flow than during spring snowmelt and summer base flow, accounting for 44% and 48% of DOC in No Name Creek and Washington Creek, respectively. The hydrophilic fraction was enriched during winter in No Name Creek and Washington Creek, accounting for 29% and 27% of DOC, respectively, when compared to spring snowmelt (17%) and summer (16%) Table 5.

[23] Fraction-specific SUVA₂₅₄ values for hydrophobic acids and hydrophilic compounds also varied across seasons (Table 4). In both No Name Creek and Washington Creek, SUVA₂₅₄ values for the hydrophobic acid fraction were lowest during winter (3.4 L mgC m⁻¹), highest during spring snowmelt (4.4 L mgC m⁻¹), and intermediate during summer (3.9 – 4.0 L mgC m⁻¹). We observed different seasonal patterns of SUVA₂₅₄ values for the hydrophilic fraction between

Table 3. Seasonal Variation in Mean DOC and SUVA₂₅₄ Values for Study Streams^a

	Winter DOC (mgC L ⁻¹)	Spring DOC (mgC L ⁻¹)	Summer DOC (mgC L ⁻¹)	Winter SUVA (L mgC ⁻¹ m ⁻¹)	Spring SUVA (L mgC ⁻¹ m ⁻¹)	Summer SUVA (L mgC ⁻¹ m ⁻¹)
Cobble Creek	-	5.3 (1) ^b	4.7 ± 2.6 (5)	-	2.9 (1)	1.1 ± 0.3 (5)
Dalton Central Creek	1.5 (1)	15.1 (1)	9.9 ± 0.5 (7)	2.6 (1)	4.2 (1)	4.1 ± 0.3 (5)
Dalton North Creek	3.6 (1)	8.2 (1)	5.8 ± 1.7 (4)	2.7 (1)	3.2 (1)	2.0 ± 0.8 (2)
Dietrich River	-	7.5 (1)	4.6 ± 2.1 (5)	-	3.5 (1)	1.5 ± 0.4 (5)
Fish Creek	1.6 (1)	-	7.7 ± 2.6 (4)	2.5 (1)	-	2.2 ± 0.5 (4)
Fort Hamlin Hills Creek	3.9 (1)	28.9 (1)	15.6 ± 2.4 (4)	3.0 (1)	3.8 (1)	4.2 ± 0.2 (5)
Gold Creek	-	-	6.1 ± 0.9 (4)	-	-	2.6 ± 0.3 (4)
Hess Creek	0.4 (1)	28.8 (1)	26.5 ± 2.0 (5)	3.0 (1)	3.9 (1)	3.4 ± 0.3 (5)
Jim River	-	-	4.4 ± 0.9 (4)	-	-	2.5 ± 0.3 (4)
Middle Fork, Koyukuk River	1.1 (1)	10.3 (1)	2.6 ± 0.4 (4)	2.1 (1)	3.7 (1)	1.8 ± 0.3 (4)
No Name Creek	5.0 ± 2.5 (2)	20.9 (1)	25.5 ± 2.2 (5)	3.2 ± 0.2 (1)	4.0 (1)	4.1 ± 0.1 (5)
Parks Creek	-	41.7 (1)	27.3 ± 2.2 (13)	-	4.1 (1)	2.6 ± 0.4 (7)
Prospect Creek	-	-	13.0 ± 6.2 (2)	-	-	0.7 (1)
Tatalina River	4.0 (1)	27.3 (1)	17.7 ± 1.7 (3)	2.7 (1)	3.9 (1)	3.7 ± 0.2 (3)
Tolovana River	8.7 (1)	24.4 (1)	16.9 ± 1.7 (5)	2.6 (1)	3.8 (1)	3.6 ± 0.1 (5)
Washington Creek	7.2 (1)	25.2 (1)	14.2 ± 2.6 (5)	3.0 (1)	3.9 (1)	3.5 ± 0.3 (5)

^aDOC, dissolved organic carbon; SUVA₂₅₄, specific ultraviolet absorbance.

^bValues in parentheses represent ± 1 standard error.

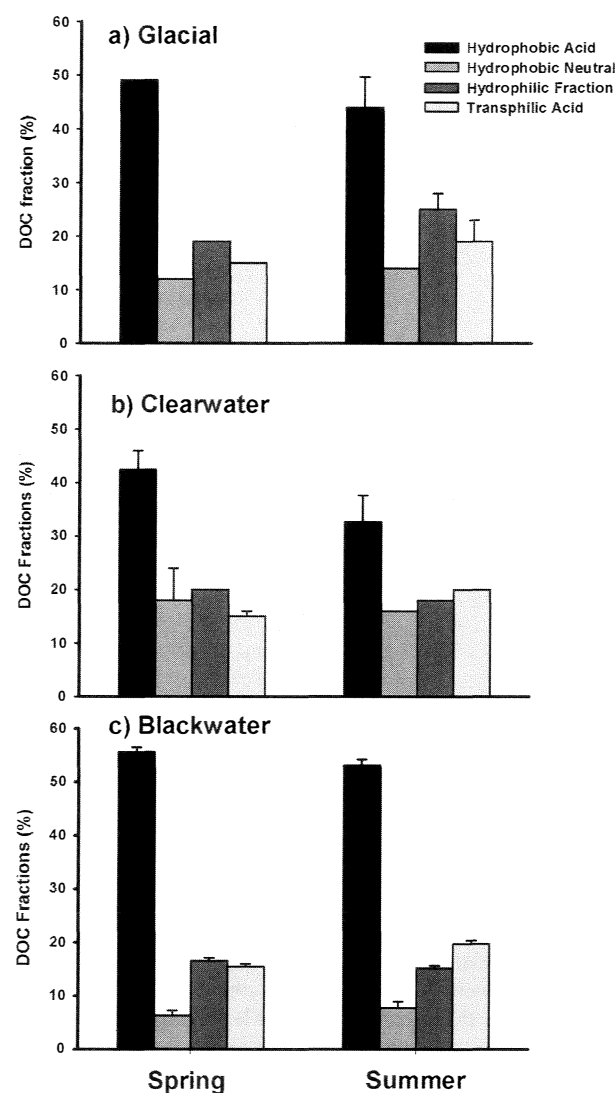


Figure 4. Seasonal variation in chemical fractions of DOC in (a) glacial, (b) clearwater, and (c) blackwater streams.

the two streams. In No Name Creek, $SUVA_{254}$ for the hydrophilic fraction was 2.5 L mgC m^{-1} during winter, increased during spring snowmelt to 3.5 L mgC m^{-1} , and was lowest during summer base flow (2.0 L mgC m^{-1}). In Washington Creek, $SUVA_{254}$ for the hydrophilic fraction

was the same during winter base flow and spring snowmelt (2.4 L mgC m^{-1}) and relatively higher during summer base flow (4.2 L mgC m^{-1}).

3.4. Seasonal Variation in DOC Fluorescence

[24] Using PARAFAC analyses of fluorescence EEMs, we identified the dominant fluorescing components within the DOM pool and quantified distinct seasonal shifts in the proportion of individual components. The percent contribution of components C2 (an oxidized quinone) and C4 (a reduced hydroquinone) composed the majority of the fluorescence signal for all samples, averaging $18.6\% \pm 0.2\%$ and $20.0\% \pm 0.4\%$, respectively (Table 5). The contribution of C2 and C4 did not vary across seasons or stream types (blackwater, clearwater, glacial streams). Components C8 and C13, which have fluorescence characteristics that resemble the amino acids tryptophan and tyrosine, composed a smaller proportion of DOM fluorescence. The proportion of C8 and C13 (added together to reflect percent protein) varied seasonally in the blackwater streams (Table 5), accounting for $8.6\% \pm 2.4\%$ during winter, $3.1\% \pm 0.2\%$ during spring snowmelt, and $2.7\% \pm 0.1\%$ during summer base flow. FI was generally highest during winter, reflecting DOM of microbial origin, and lowest during spring snowmelt, reflecting DOM of terrestrial origin. We observed intermediate FI values during summer base flow, presumably reflecting mixing of microbially and terrestrially derived DOM. We also observed a significant negative correlation between FI and $SUVA_{254}$ of the hydrophobic acid fraction ($R^2 = 0.91$, $P < 0.0001$; Figure 5). During snowmelt, FI averaged 1.3, which was close to the Suwannee River terrestrial end-member (FI = 1.23) [McKnight *et al.*, 2001]. Hydrophobic acids during snowmelt were highly aromatic, with $SUVA_{254}$ values near or above 4.0 L mgC m^{-1} (Table 4). FI and $SUVA_{254}$ of hydrophobic acids during winter and summer base flow were more variable, reflecting a mixture of terrestrial and microbial organic matter sources.

3.5. Source Water Controls on DOC Chemistry

[25] The DOC:DON ratio was negatively correlated with PC axis 1 ($R^2 = 0.26$, $P = 0.025$), suggesting that long, slow flow paths through deep groundwater may contribute relatively more DON than shallow surficial flow paths to streamflow (Figure 6a). $SUVA_{254}$ was also negatively correlated with PC axis 1 ($R^2 = 0.30$, $P < 0.0001$), suggesting hydrologic inputs for shallow groundwater contribute DOC that is relatively more aromatic than the DOC from deeper groundwater sources (Figure 6b). Finally, FI was positively correlated with PC axis 1 ($R^2 = 0.46$, $P = 0.0006$), suggesting

Table 4. Seasonal Variation in the Major Chemical Fractions of DOC and the $SUVA_{254}$ Values of Those Fractions From No Name Creek and Washington Creek

	No Name Creek			Washington Creek		
	Winter	Spring	Summer	Winter	Spring	Summer
Hydrophobic acids (%)	44	49	53	48	56	53
$SUVA_{254}$ of Hydrophobic acids (L mgC m^{-1})	3.4	4.4	4.0	3.4	4.4	3.9
Hydrophilic fraction (%)	6	10	8	2	4	8
$SUVA_{254}$ of hydrophilic fraction (L mgC m^{-1})	2.5	3.5	2.0	2.4	2.4	4.2
Transphilic acids (%)	16	18	21	15	15	18
$SUVA_{254}$ of transphilic acids (L mgC m^{-1})	2.4	3.0	2.8	2.3	3.1	2.8

Table 5. Seasonal Variation in Fluorescence Components from PARAFAC Model^a

	C1 (%)	C2 (%)	C3 (%)	C4 (%)	C5 (%)	C6 (%)	C7 (%)	C8 (%)	C9 (%)	C10 (%)	C11 (%)	C12 (%)	C13 (%)	Protein (%)	Fluorescence Index	Redox Index
<i>Fort Hamlin Hills</i>																
Winter	9	19	4	21	6	7	7	1	3	4	8	8	3	4	1.44	0.503
Spring	11	18	3	23	8	10	5	0	1	4	8	6	3	3	1.25	0.545
Summer	10	19	4	22	7	8	6	0	2	4	8	7	2	3	1.34	0.528
<i>Hess Creek</i>																
Winter	8	15	3	21	4	2	3	8	1	5	7	10	12	20	1.28	0.467
Spring	11	18	3	22	7	9	6	1	2	4	8	7	3	3	1.30	0.530
Summer	10	19	4	21	7	9	6	0	2	4	8	7	3	3	1.35	0.513
<i>No Name Creek</i>																
Winter	8	18	4	19	4	7	5	3	2	6	9	10	6	9	1.40	0.451
Spring	10	18	4	22	7	9	6	1	2	4	8	8	3	4	1.32	0.524
Summer	10	19	4	22	7	9	6	0	2	4	8	7	3	3	1.32	0.531
<i>Tatalina River</i>																
Winter	8	20	5	19	5	6	8	2	3	5	8	9	2	5	1.49	0.487
Spring	11	18	3	22	8	10	6	0	2	4	8	6	3	3	1.31	0.533
Summer	11	20	4	21	7	8	7	0	2	4	7	6	2	2	1.35	0.525
<i>Washington Creek</i>																
Winter	10	18	4	19	5	7	6	3	2	5	8	9	5	7	1.40	0.473
Spring	12	19	3	22	8	9	6	0	1	4	8	6	3	3	1.31	0.528
Summer	9	20	4	22	6	8	7	1	2	4	8	8	2	3	1.38	0.513
<i>Average</i>																
Winter	9	18	4	20	5	6	6	3	2	5	8	9	6	9	1.40	0.476
Spring	11	18	3	22	8	9	6	0	2	4	8	7	3	3	1.30	0.532
Summer	10	19	4	22	7	8	6	0	2	4	8	7	2	3	1.35	0.522

^aComponents are presented as percent relative contribution or relative abundance.

that hydrologic inputs from shallow groundwater contributes DOC with a strong terrestrial signature. Conversely, DOC from deeper groundwater sources has a weaker terrestrial signal because of microbial modification of terrestrial DOM sources, sorption of DOM to aquifer solids, or the contribution of microbially derived DOM (Figure 6c).

4. Discussion

4.1. Source Water and Seasonal Effects on DOC Composition

[26] The contribution of different source waters to streamflow governs spatial and temporal variability in stream chemistry within and across streams. In our study streams, the chemical composition of surface water reflects the hydrologic mixing of water from shallow subsurface flow paths in contact with surficial soils and deeper flow paths in contact with mineral soil and bedrock (Figure 2). Using summer base cation chemistry and PCA, we were able to identify the relative importance of shallow groundwater flowing through the active layer versus deep groundwater on streamflow generation (Figure 2). The relative influence of these two water sources varied across stream types, with relatively high inputs from deep groundwater to clearwater and glacial streams and relatively high inputs from shallow groundwater to blackwater streams. Shallow groundwater flow paths are primarily associated with moss, leaf litter, and decomposed humic material, and are perched by seasonal ice and/or permafrost. Soil leachates from surface organic material in the Yukon basin are generally aromatic and enriched in lignin phenols [Spencer *et al.*, 2008]. As a result, not only was DOC con-

centration higher in blackwater streams, but its composition was also more aromatic (i.e., higher SUVA₂₅₄ values) than that in clearwater or glacial streams during summer base flow (Figure 3). Interestingly, variations in DOC concentrations and aromaticity were fairly consistent within a stream source water class across the interior region of Alaska (500 km), with seasonal changes dominating the variability across sites (Figure 3).

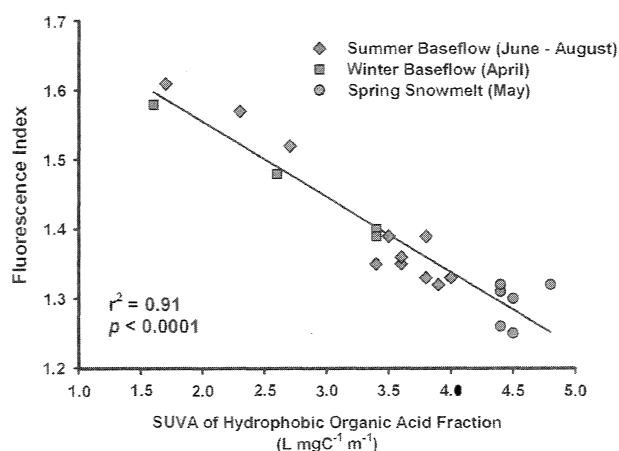


Figure 5. Linear regression between fluorescence index (FI) and SUVA₂₅₄ of hydrophobic acid fraction across three sampling periods in blackwater streams.

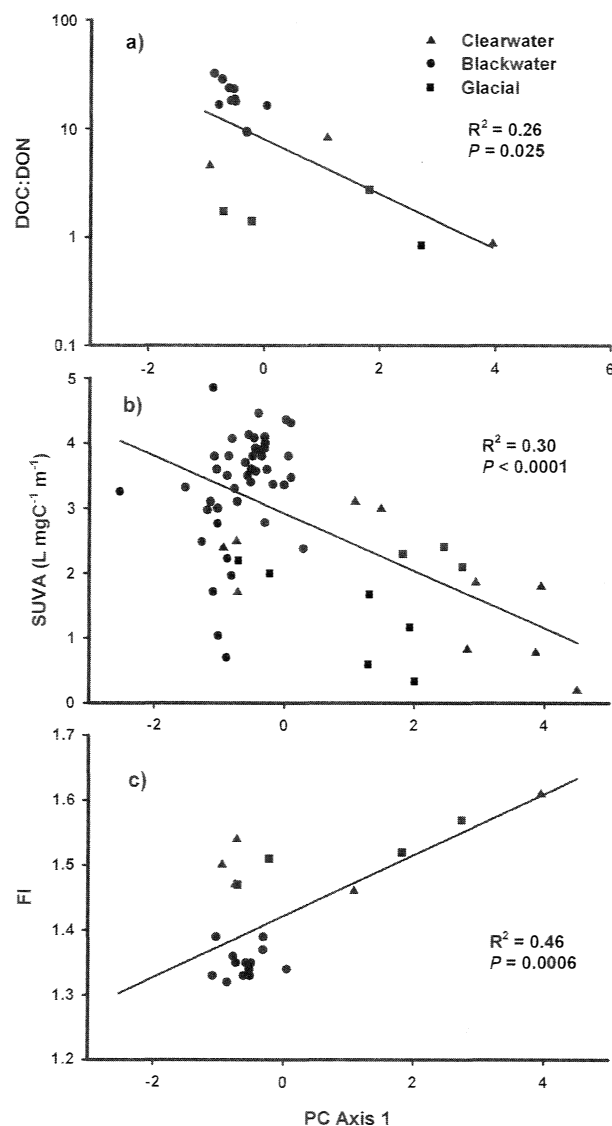


Figure 6. Results from linear regression between (a) DOC: dissolved organic nitrogen (DON) ratio, (b) SUVA_{254} , and (c) FI and PC axis 1.

[27] Our findings indicate that the concentration and composition of DOC in the streams of the Yukon basin are strongly dependent on the sources of water flowing in the stream. DOC concentration peaked during snowmelt, which is consistent with other studies in the boreal forests of interior Alaska [Petrone *et al.*, 2006; Striegl *et al.*, 2005, 2007], northern Sweden [Laudon *et al.*, 2004], western Canada [Carey, 2003], and Siberia [Cauwet and Sidorov, 1996]. During snowmelt, when groundwater inputs to streamflow are negligible, stream DOC composition was dominated by highly aromatic hydrophobic acids (Figures 4 and 5). Using fluorescence techniques, we showed the majority of DOC during spring snowmelt is of terrestrial origin ($\text{FI} < 1.4$; see McKnight *et al.* [2001]; Figure 5). Rapid inputs of allochthonous DOM to streams during snowmelt are generally

dominated by hydrophobic acids [Sebestyen *et al.*, 2008], contain large quantities of aromatic carbon, and are low in nitrogen content [Aiken and Cotsaris, 1995]. Our findings are also consistent with Spencer *et al.* [2008], who observed high concentrations of lignin phenols in Yukon basin streams during snowmelt. During snowmelt, stream DOC generally resembles the DOM source (e.g., moss, litter), because the flow path contact time between the terrestrial and aquatic ecosystem is relatively short [Sebestyen *et al.*, 2008], as the majority of subsurface flow is routed through shallow organic horizons. However, DOM leachates from boreal moss typically contain high proportions of hydrophilic compounds (~40–70%) [Kane *et al.*, 2006; Wickland *et al.*, 2007], which were not evident in streamflow during spring or summer (~20% hydrophilics; Figure 4). This suggests that hydrophilic compounds may be rapidly mineralized along lateral flow paths to the stream, which is supported by other studies in boreal and arctic regions [Michaelson *et al.*, 1998; Wickland *et al.*, 2007]. During winter base flow, the flow path contact time increases as subsurface flow is routed through deeper mineral soil horizons, and the DOM composition reflects alteration through both microbial degradation and physical adsorption processes [Cronan and Aiken, 1985; Sebestyen *et al.*, 2008]. From our study, we observed that DOC composition during winter was less aromatic (lower SUVA_{254}) with a lower proportion of hydrophobic acids and a higher proportion of hydrophilic compounds, which is consistent with selective depletion of aromatic compounds, such as lignin phenols, in the subsurface [Cronan and Aiken, 1985; Spencer *et al.*, 2008].

4.2. Implications of Permafrost Thaw for Stream DOC Chemistry

[28] Thawing of permafrost may influence groundwater inputs and DOC exports to streams in the Yukon River basin [Walvoord and Striegl, 2007]. Ice-rich permafrost restricts infiltration of precipitation, confining subsurface flow to shallow organic soil horizons [Woo, 1986]. However, as permafrost degrades and the active layer deepens, precipitation can infiltrate more deeply into the subsurface resulting in increased groundwater flow to streams. Striegl *et al.* [2005] hypothesized that permafrost thaw would cause a decrease in DOC export and an increase in export of DIC by increasing both the hydraulic residence time of water and the mineralization rates of DOC in the catchment. Walvoord and Striegl [2007] predicted a 9%–11% reduction in DOC export in the Yukon River by 2050, primarily due to the degradation of permafrost and subsequent effects on watershed hydrology. Our findings support the notion that increased groundwater contributions to streamflow will result in decreased DOC export in streams, as evidenced by the low DOC concentration in winter base flow and in clearwater streams. Furthermore, on the basis of our measurements, permafrost thaw and subsequent increases in groundwater flow path contact time will likely alter the chemical composition of DOC in streams. Our observations suggest that increased groundwater contribution to streamflow will result in lower DOC:DON ratios (Figure 6a), decreased aromaticity of stream DOC (Figure 6b), and a depletion of hydrophobic acids in favor of hydrophilic compounds (Figure 4). Lower DOC:DON ratios may result from longer, slower groundwater flow

paths, where microbial degradation of DOC and leaching of N-rich DOM from mineral soils can increase relative N content of DOM [Hood *et al.*, 2005; Sebestyen *et al.*, 2008; Balcarczyk *et al.*, 2009]. Depletion of aromatic C and hydrophobic acids following permafrost thaw may result from sorption of hydrophobic DOM to mineral soil particles or the increased microbial degradation of DOM as flow path contact time increases [Cronan and Aiken, 1985].

[29] Large stocks of old (Holocene- and Pleistocene-aged) carbon are also stored in permafrost [Zimov *et al.*, 2006; Tarnocai *et al.*, 2009], which, upon thaw, may result in the transfer of significant amounts of old DOC to rivers. A number of recent studies have used radiocarbon ($\Delta^{14}\text{C}$) to evaluate changes in the age, turnover, and origin of DOC exported to arctic rivers [Guo and Macdonald, 2006; Neff *et al.*, 2006; Raymond *et al.*, 2007]. More than 50% of DOC exported during snowmelt is 1–5 years old, suggesting that DOC during spring snowmelt is relatively young and labile [Raymond *et al.*, 2007; Holmes *et al.*, 2008]. As summer progresses and the active layer thaws, older DOC is transferred to rivers from deeper soil horizons within the active layer [Neff *et al.*, 2006]. Our findings showed that DOC during summer base flow is less aromatic than during spring snowmelt (Table 3 and Figure 3), which is consistent with the presence of organic matter from deeper soil horizons. We also showed that FI index increases from snowmelt to summer base flow (Figure 5), indicating that DOC during summer is a mixture of deeper terrestrial and microbial organic matter sources. However, we did not observe significant differences in the major chemical fractions of DOC during summer base flow.

5. Conclusions

[30] Changes in watershed hydrology following permafrost degradation in high-latitude watersheds will undoubtedly alter the flux and composition of DOM from terrestrial to aquatic ecosystems. Wildfire in the boreal region will likely exacerbate permafrost degradation [Yoshikawa *et al.*, 2002], but it remains unclear how the interaction between fire and permafrost will affect DOM chemistry in northern watersheds. The nature and magnitude of DOM transformations along subsurface flow paths to streams remains a considerable uncertainty in watershed studies and is currently an important area of focus [Sebestyen *et al.*, 2008]. Microbial mineralization is often governed by the chemical composition of DOM [Wickland *et al.*, 2007; Fellman *et al.*, 2009; Balcarczyk *et al.*, 2009; Holmes *et al.*, 2008] and is an important feedback to climate warming at high latitudes [Kling *et al.*, 1991]. Prior studies indicate that the proportion of hydrophilic and proteinaceous compounds is significantly correlated with rates of DOM mineralization [Qualls and Haines, 1992; Michaelson *et al.*, 1998; Balcarczyk *et al.*, 2009]. In our study, the proportion of hydrophilic and proteinaceous compounds was elevated during winter, when source water contributions from deep groundwater dominated streamflow. These observations suggest that future permafrost degradation and higher contributions of groundwater to streamflow may result in a higher fraction of labile DOM in streams of the Yukon River basin. Furthermore, northern rivers across the arctic and subarctic may be, in

general, susceptible to changes in watershed hydrology and DOM dynamics following degradation or loss of permafrost.

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