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Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost

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Abstract We examined the impact of permafrost on dissolved organic matter (DOM) composition in Caribou-Poker Creeks Research Watershed (CPCRW), a watershed underlain with discontinuous permafrost, in interior Alaska. We analyzed long term data from watersheds underlain with varying degrees of permafrost, sampled springs and thermokarsts, used fluorescence spectroscopy, and measured the bioavailabity of dissolved organic carbon (DOC). Permafrost driven patterns in hydrology and vegetation influenced DOM patterns in streams, with the stream draining the high permafrost watershed having higher DOC and dissolved organic nitrogen (DON) concentrations, higher DOC:DON and greater specific ultraviolet absorbance (SUVA) than the streams draining the low and medium permafrost watersheds. Streams, springs and thermokarsts exhibited a wide range of DOC and DON concentrations (1.5–37.5 mgC/L and 0.14–1.26 mgN/L, respectively), DOC:DON (7.1–42.8) and SUVA (1.5–4.7 L mgC^{-1} m^{-1}). All sites had a high proportion of humic components, a low proportion of protein components, and a low fluorescence index value (1.3–1.4), generally consistent with terrestrially derived DOM. Principal component analysis revealed distinct groups in our fluorescence data determined by diagenetic processing and DOM source. The proportion of bioavailable DOC ranged from 2 to 35%, with the proportion of tyrosine- and tryptophan-like fluorophores in the DOM being a major predictor of DOC loss ($p < 0.05$, $R^2 = 0.99$). Our results indicate that the degradation of permafrost in CPCRW will result in a decrease in DOC and DON concentrations, a decline in DOC:DON, and a reduction in SUVA, possibly accompanied by a change in the proportion of bioavailable DOC.

Keywords Bioavailability · Boreal forest · Discontinuous permafrost · Dissolved organic matter · Fluorescence · Thermokarst

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Introduction

Dissolved organic carbon (DOC) constitutes the largest pool of organic carbon in most streams. DOC serves as a microbial energy source (Findlay et al.

1993; Baker et al. 2000; Raymond and Bauer 2000), influences the availability of nutrients (Qualls and Haines 1991), affects the transport and degradation of pollutants (Morris and Hargreaves 1997) and alters stream pH (McKnight et al. 1985). DOC transport in streams is also an important pathway for carbon loss from terrestrial ecosystems. In headwater streams of the boreal forest, DOC originates primarily from allochthonous (terrestrial) sources (Boyer et al. 1996). Allochthonous DOC is transported to streams from a number of sources including ground water, soil water, riparian zones and overland flow (Hood et al. 2005). Stream DOC derived from these different sources can have unique chemical characteristics, which influence its use by microbes (Michaelson et al. 1998; Kalbitz et al. 2000; Kawahigashi et al. 2004).

Much of the northern boreal forest is underlain with discontinuous permafrost, which has a large effect on catchment hydrology and the resulting delivery of dissolved organic matter (DOM) to streams (MacLean et al. 1999). In areas underlain with permafrost, flow is largely restricted to organic horizons and leaches DOM from soil. In areas lacking permafrost, flow can infiltrate into deeper organic layers and mineral soil where DOM can be adsorbed and/or consumed by microbes (MacLean et al. 1999; Carey 2003). Increased contact time with mineral soil in watersheds lacking permafrost decreases the concentration and alters the composition of DOM that reaches a stream (Kawahigashi et al. 2004). Thus, streams draining catchments underlain with permafrost typically have a higher concentration of DOM and DOM that is chemically different from DOM in streams draining catchments lacking permafrost (MacLean et al. 1999; Kalbitz et al. 2000; Carey 2003). Discontinuous permafrost in the boreal forest of Alaska is thawing in response to climatic warming, which, in turn, is influencing the movement of dissolved material from upland soils to streams by altering watershed hydrology and vegetation (Striegl et al. 2005). In the Caribou-Poker Creeks Research Watershed (CPCRW) in interior Alaska over a third of the permafrost is just below 0°C, and at least 2% of the permafrost was lost during the 20th century (Hinzman et al. 2005). As ice-rich permafrost thaws, topographic depressions (thermokarsts) can form and may act as a source of DOC to streams.

Although a number studies have been done concerning the concentration and flux of DOM in streams draining catchments underlain with discontinuous permafrost, the influence of permafrost on the composition and bioavailability of DOM in these streams has not been well studied. In our study, we addressed the following question in catchments underlain with varying degrees of permafrost: how does permafrost and the associated hydrologic flow path through the catchment affect DOM concentration and quality in streams? We hypothesized that the chemical composition of DOM in waters flowing from different watershed flowpaths would differ due to the presence of absence of permafrost and the resulting confinement of flowpaths to organic horizons or the potential for deeper infiltration. These differences in the flow of water through catchments will, in turn, affect stream water DOM concentration, substrate quality and bioavailability. In order to test this hypothesis, we used three approaches. First, longer-term stream chemistry and hydrologic data from streams draining a low, medium and high permafrost watershed were analyzed for variation in DOM concentration, composition and response to changes in discharge. Second, fluorescence spectroscopy was used in combination with longer-term indicators of DOM quality to determine the composition of DOM in streams, springs and thermokarsts. Finally, we used a laboratory mesocosm experiment to establish if differences in DOM composition influence the bioavailability of DOC in streams, springs and thermokarsts.

Methods

Study site

Our study was conducted in the CPCRW, which is located approximately 50 km NE of Fairbanks, Alaska (65.15°N, 147.5°W) and is approximately 104 km^2 in size. The climate of CPCRW is continental, with warm summers (mean = 16.4°C in July), cold winters (mean = − 29°C in January), and low precipitation (411 mm, of which 31% falls as snow; Haugen et al. 1982). The watershed is located in a region of discontinuous permafrost, with the extent of permafrost underlying sub-catchments ranging from 4 to 53%. The distribution of permafrost in interior Alaska is largely a function of aspect and winter temperature, with north-facing slopes and valley

bottoms generally underlain by permafrost (Viereck et al. 1983).

Vegetation types in the watershed are typical of interior Alaska. South facing slopes are dominated by hardwood forests of paper birch (*Betula paprifera*) and quaking aspen (*Populous tremuloides*), whereas north facing slopes are dominated by black spruce (*Picea mariana*), white spruce (*P. glauca*) and feathermoss (*Pleurozium schreberi*). Soil in the valley bottoms is covered with mosses (*Sphagnum spp., Hylocomium*) and dwarf shrubs *(B. nana, Salix spp., Vaccinium uliginosum*), with a patchy coverage of alder (*Alnus tenuifolia*).

For this study, data were used from four streams draining catchments that varied in permafrost coverage and size: C2 (4% permafrost and 5.2 km^2), C4 (19% permafrost and 10.4 km^2), C3 (53% permafrost and 5.7 km^2) and CJ (28% permafrost and 41.7 km^2, Fig. 1; Table 1). The C4 catchment was partially burned in 1999 by a prescribed fire to assess fire and climate feedbacks in the boreal forest (FROSTFIRE project, Hinzman et al. 2003). The prescribed burn was of moderate intensity, covered 28% of the watershed area, and was largely restricted to the black spruce-dominated north-facing slopes with the riparian zone left mostly unburned. CJ is below the confluence of C2, C3, C4 and several other streams. In addition, we sampled two springs in the C3 watershed (S-C3a and S-C3b), one spring in the C4 watershed (S-C4a) and two thermokarsts located near the CJ sampling station (K1 and K2, Fig. 1). The thermokarst samples were collected from water flowing from the topographic depressions that formed from the thawing of permafrost.

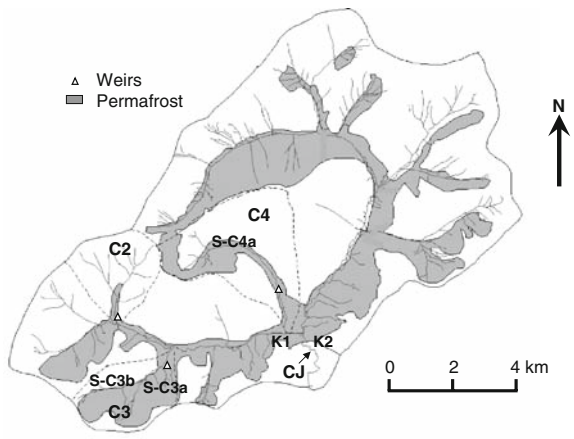

Fig. 1 Map of the Caribou-Poker Creeks Research Watershed with sampling sites. Indicated on the map are the locations of stream (C), springs (S), and thermokarsts (K) sampling sites

Table 1 Stream and watershed characteristics in Caribou Poker Creeks Research Watershed

Watershed/ stream	Stream length (km)	Basin area (km^2)	Permafrost coverage (%)	Aspect
C2	2.2	5.2	4	S
C3	2.6	5.7	53	NE
C4	5	10.4	19	SSE
CJ	19	41.7	28	E

Field methods

In June through August of 2002–2006 stream water samples were collected daily from C2, C4 and C3 using autosamplers. Additionally, in 2006 weekly grab samples were collected from all streams, springs and thermokarsts. Spring and thermokarst samples were collected at the point of discharge from the ground, where water reaches the surface, so that they were minimally influenced by surface biotic and abiotic transformation. Samples were collected in acid-washed 125 ml high density polyethylene (HDPE) bottles and filtered within 24 h using glass fiber filters (Gelman A/E, 0.7 μm pore size). Samples were refrigerated until analysis (<48 h). Cation samples were frozen until processing. We found no significant difference in chemistry between autosampler and grab samples.

From 2002 to 2006, stream stage height was measured continuously from June through August using pressure transducers and Campbell Scientific dataloggers (CR10X) at Parshall flumes in the C2, C3 and C4 streams. For each stream, rating curves were developed to translate stage height to discharge.

Laboratory analyses

Samples were analyzed for DOC, dissolved organic nitrogen (DON), DOC:DON, specific ultraviolet absorbance (SUVA) and DOC fluorescence. In the laboratory, electrical conductance was measured using an accument portable ASPSO conductivity meter. DOC concentration was measured as non-purgeable organic carbon using a Shimadzu TOC 5000 analyzer

plumbed to an Antek 7050 nitric oxide chemiluminescent detector to quantify total dissolved nitrogen (TDN). Anions (Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}) and cations (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+) were determined using a Dionex DX-320 Ion Chromatograph. Dissolved organic nitrogen (DON) was calculated as TDN—($NH_4^+ + NO_3^- + NO_2^-$). Nitrite levels were always at or below detection limits. SUVA is defined as UV absorbance at $\lambda = 254$ nm divided by DOC concentration (mg/L) and is a measure of DOM aromaticity (Weishaar et al. 2003). SUVA was quantified using a Beckman DU 640B spectrophotometer set to $\lambda = 254$ nm and a 1-cm cell path.

DOC optical properties

In 2006, 100 ml grab samples were collected from streams, springs S-C3a and S-C3b, and thermokarsts in pre-rinsed amber HDPE bottles for fluorescence analysis and sent to Florida International University within 48 hours for analysis. Bulk water samples were submitted for fluorescence and UV-Vis absorption analyses after filtration using standard procedures reported in the literature (McKnight et al. 2001; Jaffé et al. 2004). UV–Vis absorption spectra were measured with a Shimadzu UV-2102PC spectrophotometer between 250 and 800 nm in a 1 cm quartz cuvette to determine UV absorbance at 254 nm ($SUVA_{254}$).

Fluorescence spectra were determined with a Horiba Jobin Yvon Fluoromax-3 spectrofluorometer equipped with a 150 W continuous output xenon arc lamp (Maie et al. 2006). Single emission fluorescence scans were obtained at an excitation wavelength of 370 nm and the fluorescence intensity was recorded at emission wavelengths ranging from 385 to 500 nm. The band pass was set at 5 nm for excitation and emission wavelengths. The fluorescence index (FI) was calculated using the ratio of fluorescence intensities at 470 and 520 nm (Cory and McKnight 2005). The FI was used to distinguish whether DOM was derived from aquatic microbial material or terrestrial material with a difference of at least 0.1 being indicative of a difference in the source of DOM (McKnight et al. 2001). Excitation-Emission Matrices (EEMs) were determined at excitation wavelengths (λ_{ex}) between 240 and 455 nm at 5 nm intervals. The emission wavelengths were scanned from $\lambda_{ex} + 10$ nm to $\lambda_{ex} + 250$ nm at 2 nm intervals. The sample (emission signal, S) and reference (excitation lamp output, R) signals of the fluorescence spectra were collected and the ratio (S/R) was calculated. Post acquisition, several steps were taken to correct the fluorescence spectra. First, an inner filter correction was applied to the fluorescence data according to McKnight et al. (2001). After inner filter corrections, the sample EEM underwent spectral subtraction of the Milli-Q water to remove most of the effects of Raman scattering. Instrument bias due to wavelength dependent efficiencies of the specific instrument's optical components (gratings, mirrors, etc.) were then corrected by applying multiplication factors (supplied by the manufacturer) for both excitation and emission wavelengths.

Parallel-factor analysis (PARAFAC) statistically decomposes EEMs into distinct fluorescent components without any assumptions on their spectral shape or the number of components (Stedmon et al. 2003). Since the number of the spectra in our study was not large enough to run a specific PARAFAC model for this data set, we combined the EEMs from our study with an already existing database of over 2000 EEMs. For PARAFAC modeling, EEMs with excitation wavelengths from 260 to 450 nm and emission wavelengths from 300 to 500 nm were used to minimize the influence from noise signal. The PARAFAC analysis was carried out in MATLAB (The MathWorks Inc.) software using the "N-way toolbox for MATLAB". Split-half analysis and residual analysis (Stedmon et al. 2003; Cory and McKnight 2005) were used to validate the identified components. A total of ten fluorescent components were identified (Fig. 2; Table 2).

DOC bioavailability

In June of 2007, grab samples were collected from four streams, three springs and two thermokarsts for an incubation experiment to measure DOC bioavailability. Four liters of sample were collected in acid washed cubitainers. All samples were transported in a cooler to the lab, filtered and refrigerated until analysis (<24 h).

The incubation experiment followed a factorial design that included in situ and elevated levels of temperature and nutrients. The various treatment combinations resulted in a total of four treatments: (1) 4°C with in situ nutrients (2) 4°C with nutrients added (3) room temperature with in situ nutrients, and (4) room temperature with nutrients added. Nutrients

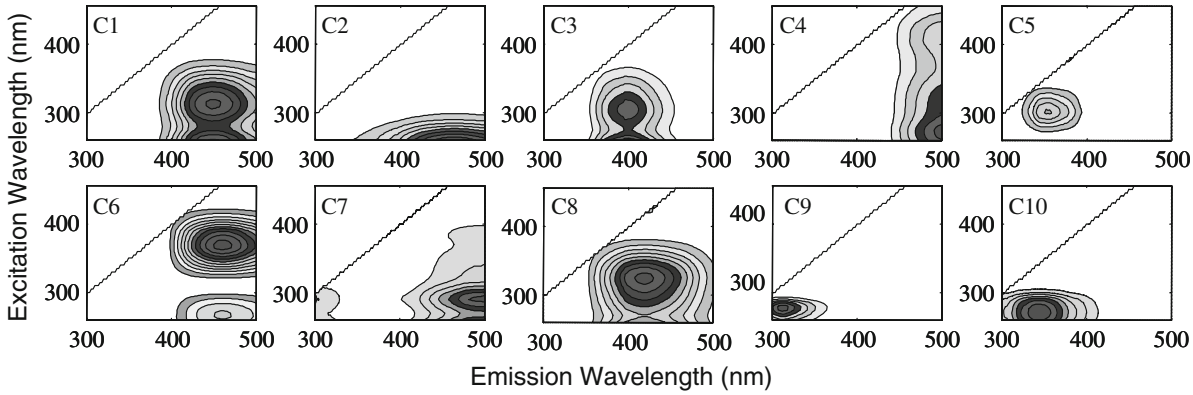

Fig. 2 Excitation-emission matrices for the PARAFAC modeled components identified in DOM in streams, springs, and thermokarsts

Table 2 Characteristics of the fluorescent components identified in the EEMs of DOM in streams, springs and thermokarsts

Component	Assignment/region			Specific comment
	Coble (1996), Coble et al. (1998)	Stedmon and Markager (2005a)	Cory and McKnight (2005)	
1	Visible-humic (peak C)	3	C10	Terrestrial origin, humic-like component; absent in wastewater (Stedmon and Markager 2005a)
2	UV-humic (peak A)	1	Q1/C11	Terrestrial origin, humic-like component; formed during photodegradation (Stedmon et al. 2007); absent in wastewater (Stedmon and Markager 2005a)
3	Marine-humic (peak M)	6	Q3**/C12 or C3	Microbial-origin, abundant in wastewater (Stedmon and Markager 2005a)
4	–	2	SQ1/C6	High in humic acids (Maie et al., unpublished data); very sensitive to microbial and photochemical degradation (Stedmon et al. 2007); decrease fluorescence index (Cory and McKnight 2005)
5	Peak N	–	–	Autochtonous, biologically labile component (Coble et al. 1998)
6	–	4	C1	Microbial processing of algae-derived DOM (Component 5; Stedmon and Markager 2005b); increase fluorescence index (Cory and McKnight 2005)
7	–	–	HQ**/C4	Microbial processing of algae-derived DOM (Component 1, Stedmon and Markager 2005b)
8	–	5	C6**	
9	Tyr (peak B)	8	Tyr/C13	Significantly weak in large protein molecules (Lakowicz 1983); Peptides (Yamashita and Tanoue 2003)
10	Trp (peak T)	7	Trp/C8	Proteins (Yamashita and Tanoue 2003)

**Components were only found in the data set collected from Antarctica and are considered to be microbial orgin

were added to elevate the nutrient concentration by 1.0 mgN/L and 0.1 mgP/L. Temperature was maintained at 4°C by placing samples in a refrigerator. Five replicates were run for each treatment combination.

For each replicate, a mason jar was filled with 190 ml of sample, and a piece of glass fiber filter was added to promote bacterial growth (Kawahigashi et al. 2004). Natural assemblages of microbes were used for incubation experiments in order to capture in situ conditions. Nutrient stock solution or nanopure water was added (10 ml), so each treatment had a final volume of 200 ml. For DOC analysis, 5 ml of sample was filtered using a peristaltic pump through 0.2 μm pore size membrane filters into vials, and

100 µl of 2 N HCl was added. DOC was measured at 0 and 40 days. Bioavailable DOC was calculated as the loss of DOC after 40 days of incubation. The 40-day incubation period was chosen to capture both the labile and more refractory portion of the DOC.

Statistical analysis

Regression analysis was used to examine relationships between stream chemistry and discharge. To compare differences in slopes among streams, *t*-tests were run on regression slopes. Analysis of Covariance (ANCOVA) was used to test for differences in average chemical concentrations among streams and years. One-way analysis of variance (ANOVA) was used to test for differences among treatments and sites in the incubation experiment. If a significant difference was found ($p < 0.05$), we used Tukey's tests to determine which sites were significantly different ($p < 0.05$).

The PARAFAC data were analyzed using principal components analysis. The PARAFAC data consisted of ten components expressed as percent of fluorescent DOM (Fig. 2; Tables 2, 4). These components were standardized into a covariance matrix such that components with greater magnitude would not exert more influence on the model than those with less magnitude. The first two PCA factor scores were further analyzed using ANOVA, and when there were significant effects Tukey's tests were used to determine significant differences among groups. Regression analysis was used to determine significant relationships between stream chemistry and the first two principal components.

Results

Hydrology

Stream discharge responses to precipitation varied among the watersheds in relation to the extent of permafrost. The stream draining the high permafrost watershed (C3) had larger and more frequent spates than the streams draining the low (C2) and medium (C4) permafrost watersheds. The summers of 2002, 2003 and 2006 were relatively high flow years compared to 2004 and 2005 with the largest and most frequent spates occurring in 2003. Mean discharge for 2002, 2003 and 2006 ranged from 24.6 to 79.4 L/s. In contrast, 2004 and 2005 were relatively low flow years with mean discharge ranging from 28.4 to 69.2 L/s.

Stream DOM concentration and quality

DOC concentration was always highest in the stream draining the watershed with the greatest extent of permafrost, whereas the streams draining the low and medium permafrost catchments had similar DOC concentrations (Fig. 3a). Mean summer DOC concentrations were 3.0, 2.9 and 6.2 mgC/L in the streams draining the low, medium and high permafrost watersheds, respectively. Comparing across

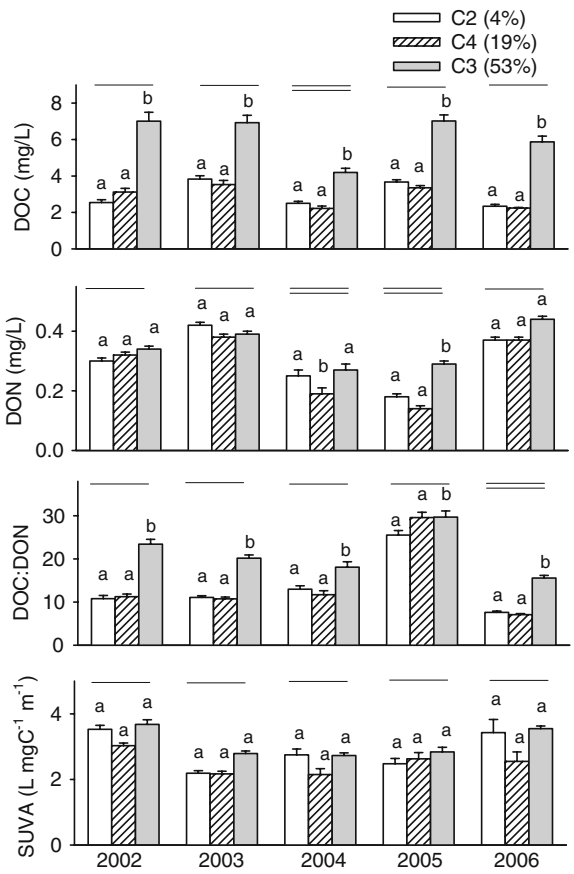

Fig. 3 DOC (**a**), DON (**b**), DOC:DON (**c**) and SUVA (**d**) for the streams draining the low, medium and high permafrost watersheds for 2002–2006. Values are means ± SE. The *letters* denote significant differences among streams for a given year ($p < 0.05$). *Single* or *double lines* above the bars denote significant differences among years in a given stream ($p < 0.05$)

years, all streams had significantly lower DOC concentration in 2004 (Fig. 3a).

Mean DON concentration was highest in the stream draining the high permafrost watershed (0.35 mgN/L) and slightly lower in the streams draining the low and medium permafrost watersheds (0.31 and 0.29 mgN/L, respectively; Fig. 3b). Among streams, DON concentration did not significantly vary in higher flow years (2002, 2003 and 2006, Fig. 3b). However, in years with lower flow (2004 and 2005) DON concentration was highest in the stream draining the high permafrost watershed (Fig. 3b). Comparing across years, DON concentration was lower in all streams during the low flow years of 2004 and 2005 (Fig. 3b).

Mean DOC:DON in the streams draining the low, medium and high permafrost watersheds was 14, 14, and 21, respectively (Fig. 3c). In most years (except 2005) DOC:DON was significantly higher in the stream draining the high permafrost watershed than in the streams draining the low and medium permafrost watersheds. DOC:DON across years was lower in 2006 in all streams (Fig. 3c). Although not significantly different, SUVA values tended to be highest in the stream draining the watershed with the greatest extent of permafrost. Mean summer SUVA in the stream draining the high permafrost watershed was 3.0 L mgC^{-1} m^{-1} followed by the streams draining the low and medium permafrost watersheds with 2.6 and 2.4 L mgC^{-1} m^{-1}, respectively (Fig. 3d).

DOC and discharge relationships

DOC concentration in all streams was positively correlated with discharge in nearly every year (Table 3). The slope of DOC versus discharge was significantly different among watersheds in all years (Table 3). The stream draining the low permafrost watershed had the largest mean slope of DOC versus discharge with 0.071 mgC s L^{-2}, followed by the streams draining the high and medium permafrost watersheds with 0.048 and 0.025 mgC s L^{-2}, respectively (Table 3). The stream draining the high permafrost watershed historically has the highest flux of DOC (8.34 kg ha^{-1} $year^{-1}$) followed by the streams draining the medium (5.32 kg ha^{-1} $year^{-1}$) and low (4.34 kg ha^{-1} $year^{-1}$) permafrost watersheds (Petrone et al. 2006).

Table 3 Slopes (mgC s L^{-2}) of DOC versus discharge for 2002–2006 for the streams draining the low, medium and high permafrost watersheds

	Stream		
	C2 (4%)	C4 (19%)	C3 (53%)
2002	0.0751*	0.0414*	0.0455*
2003	0.0137*	0.0156*	0.0352*
2004	0.1191*	0.0419*	0.0635*
2005	0.0625*	0.0105	0.0632*
2006	0.0823*	0.0246*	0.0336*
Mean slope	0.0705	0.0247	0.0482

* Statistically significant slope ($p < 0.05$). In all years, slopes were significantly different among streams ($p < 0.5$)

DOM concentration and quality in springs and thermokarsts

Springs and thermokarsts in CPCRW exhibited a wide range of DOC and DON concentrations, DOC:DON and SUVA (Fig. 4). The range of DOC and DON concentrations in springs and thermokarsts was 1.5–37.5 mgC/L and 0.29–1.26 mgN/L (Fig. 4a, b). Along with having the highest DOC and DON concentrations, thermokarsts had the highest DOC:DON and SUVA values with 42.8 and 4.7 L mgC^{-1} m^{-1}. In contrast, springs S-C3b and S-C4a had the lowest DOC:DON and SUVA values with 7.2 and 1.5 L mgC^{-1} m^{-1}, respectively (Fig. 4c, d).

DOM optical properties

All sites had similar fluorescence index values ranging from 1.3 to 1.4 (Table 4). Fluorescence index values were negatively correlated with both SUVA and DOC:DON.

The analysis of DOM fluorescence characteristics, based on EEM-PARAFAC analysis, using PCA revealed distinct differences among sites (Fig. 5). PCA identified two factors that together explained 85% of the variance in the PARAFAC data. Loadings for the first PCA axis were most strongly affected by PARAFAC components 2 and 8, both of which are terrestrial humic-like components (Fig. 5). Loadings for the second PCA axis were most strongly influenced by PARAFAC components nine and ten (tyrosine and tryptophan), and component one (terrestrial humic-like; Fig. 5). Tukey's test revealed three distinct

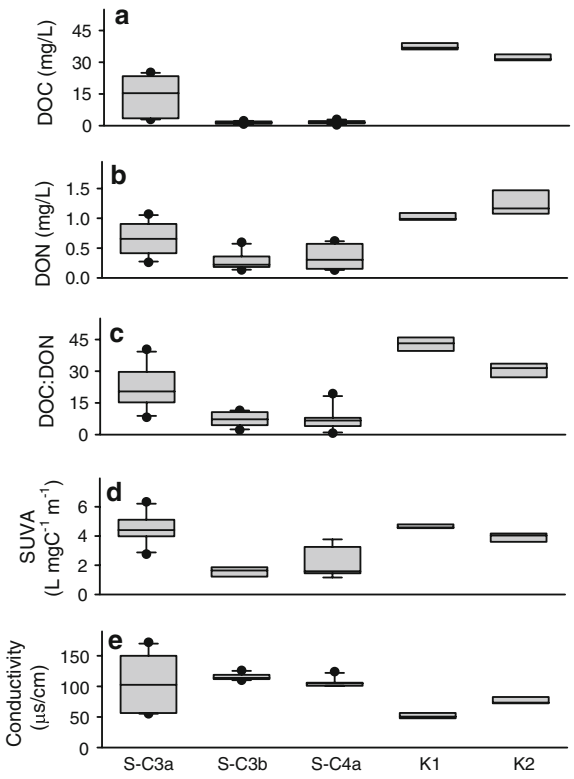

Fig. 4 DOC (**a**), DON (**b**), DOC:DON (**c**), SUVA (d) and conductivity (**e**) from springs and thermokarsts for six sampling dates in 2006. S, denotes a spring followed by the watershed in which the spring was located and K, denotes a thermokarst. The *center line*, *box extent*, *error bars* and *circles* represent the median, 25th and 75th, 10th and 90th, and 5th and 95th percentiles, respectively

groups in the PCA results, with the thermokarst samples as a separate group along PCA axis one and spring S-C3b samples as a separate group along PCA axis two (Fig. 5). Factor 1 was positively correlated with conductivity, whereas factor 2 was negatively correlated with conductivity (Figs. 6e, 7b). Factor 1 was negatively correlated with DOC, DON, DOC:-DON and SUVA (Fig. 6). Factor 2 was positively correlated with DOC:DON (Fig. 9a).

DOC bioavailability

Like DOC concentration and quality, streams, springs and thermokarsts exhibited a wide range of DOC bioavailability ranging from 2 to 35% of the initial DOC after 40 days of incubation under 4°C and in situ nutrient conditions (Fig. 8). The proportion of

Table 4 DOC fluorescence data for the 2006 biweekly stream, spring and thermokarst samples. All values are a mean (± SE) of six samples

Site	Site type	Component (%)										
		FI	1	2	3	4	5	6	7	8	9	10
C2	Stream	1.38 (0.01)	14.5 (0.9)	17.2 (0.4)	7.2 (0.4)	20.4 (0.3)	3.1 (0.0)	15.8 (0.4)	1.8 (0.1)	13.7 (0.5)	2.3 (0.4)	4.0 (0.3)
C3	Stream	1.37 (0.01)	18.4 (0.4)	17.3 (0.3)	8.0 (0.2)	20.9 (0.3)	2.8 (0.1)	15.7 (0.2)	0.9 (0.3)	11.8 (0.5)	1.4 (0.1)	2.8 (0.2)
C4	Stream	1.39 (0.01)	14.4 (0.7)	16.8 (0.4)	7.9 (0.2)	18.7 (0.2)	3.6 (0.1)	15.2 (0.3)	1.4 (0.1)	13.7 (0.7)	3.4 (0.2)	4.9 (0.4)
CJ	Stream	1.37 (0.01)	20.3 (0.5)	17.6 (0.2)	10.7 (0.4)	18.5 (0.6)	2.9 (0.1)	14.6 (0.2)	1.3 (0.1)	9.0 (0.5)	2.0 (0.4)	3.1 (0.3)
S-C3a	Spring	1.33 (0.01)	18.6 (0.3)	20.1 (0.9)	8.8 (0.6)	19.3 (0.4)	2.3 (0.2)	14.0 (0.5)	3.2 (0.4)	9.6 (0.4)	1.3 (0.3)	2.8 (0.3)
S-C3b	Spring	1.37 (0.02)	12.7 (0.7)	17.1 (0.9)	9.2 (0.8)	16.1 (0.7)	4.4 (0.3)	12.5 (0.5)	2.5 (0.4)	11.5 (0.8)	5.7 (1.2)	8.3 (0.9)
K1	Thermokarst	1.32 (0.02)	17.7 (0.6)	27.3 (1.1)	9.7 (0.5)	15.7 (0.3)	2.7 (0.2)	11.1 (0.4)	5.4 (0.4)	7.4 (0.5)	0.9 (0.2)	2.1 (0.2)
K2	Thermokarst	1.36 (0.01)	16.7 (0.4)	27.9 (0.9)	11.9 (0.6)	13.9 (0.6)	3.3 (0.2)	10.7 (0.2)	5.0 (0.1)	7.4 (0.3)	0.4 (0.2)	2.8 (0.1)

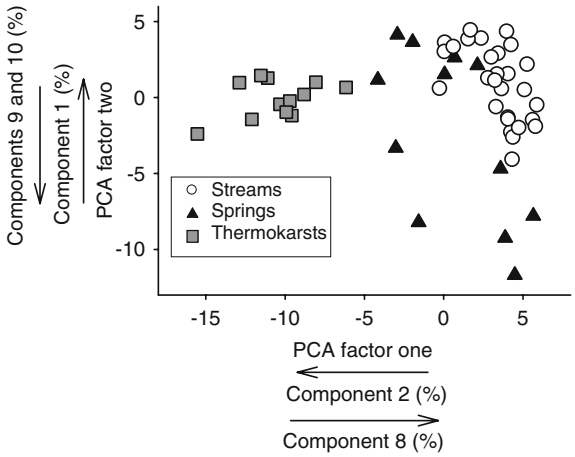

Fig. 5 The first two line vectors from the principal components analysis (PCA) using the 2006 PARAFAC data from streams (*open circles*), springs (*closed triangles*) and thermokarsts (*grey squares*). The percent of each of the 10 fluorescing DOC components was used in the model. The two axes shown explained 85% of the variance in the data

DOC lost from springs S-C3b and S-C4a was significantly higher than the proportion lost from all other sites. Despite thermokarsts having the highest DOC concentration (Fig. 4), most of the DOC was not biodegradable under the incubation conditions (Fig. 8). DOC bioavailability in stream samples was intermediate between springs and thermokarsts, with the stream draining the high permafrost watershed having the lowest proportion of DOC lost among the streams. However, DOC bioavailablity was not significantly related with DOC concentration. Temperature and nutrients had variable effects on the bioavailability of DOC (Fig. 8). In general, temperature and nutrients did not affect DOC decomposition. However, DOC loss from the stream draining the high permafrost watershed and spring S-C3a significantly increased with an increase in both temperature and nutrients. When expressed as absolute concentration, the loss of DOC after 40 days of incubation under 4°C and in situ nutrient conditions ranged from 0 to 1.1 mgC/L. The loss of DOC was significantly higher in thermokarsts than all other sites in the room temperature with in situ nutrients treatment. The percent of tyrosine and tryptophan in the sample was a major predictor of DOC loss (Fig. 9, $R^2 = 0.99$).

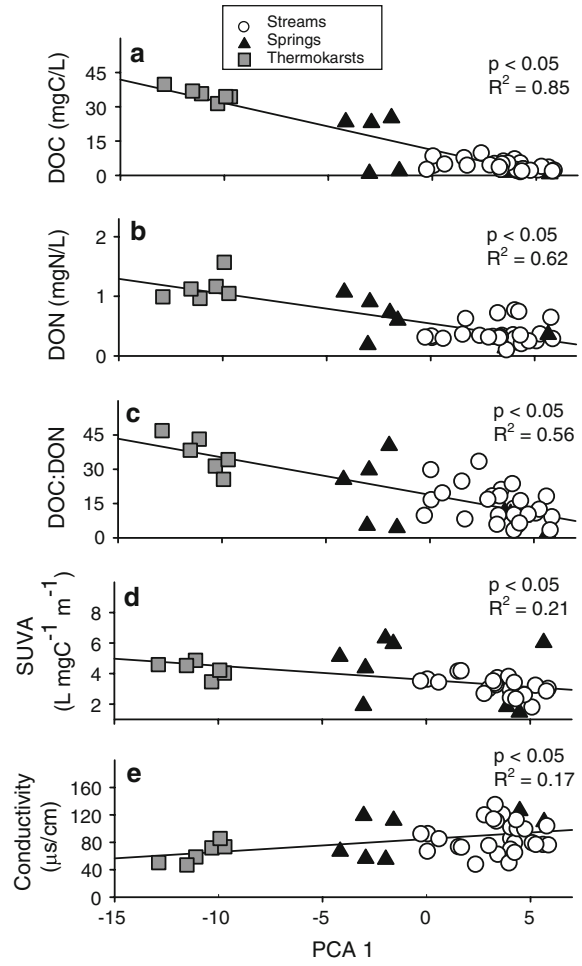

Fig. 6 Stream (*open circles*), spring (*closed triangles*) and thermokarst (*grey squares*) conductivity (**a**), DOC (**b**), DON (**c**), DOC:DON (**d**) and SUVA (**e**) versus PCA axis one. All relationships were significant ($p < 0.05$)

Discussion

Permafrost, hydrology and DOM composition

The indicators of DOM quality (DOC:DON and SUVA) suggest that even though the stream draining the high permafrost watershed had a greater concentration of DOM than the streams draining the low and medium permafrost watersheds, the DOM may be of lower quality. As we hypothesized, differing hydrologic flowpaths through the watershed resulted in differences in stream water chemistry. The differences in DOM chemistry among streams may be a result of plant litter chemistry, decomposition stage,

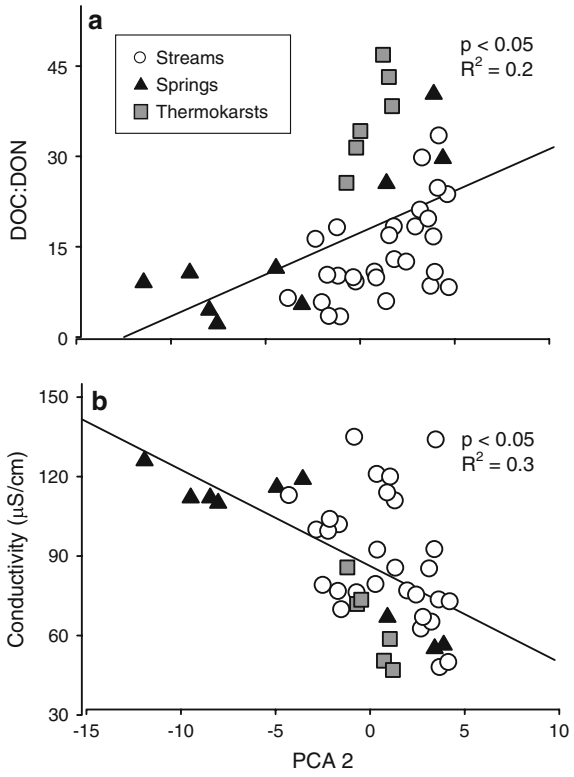

Fig. 7 Stream (*open circles*), spring (*closed triangles*) and thermokarst (*grey squares*) conductivity (**a**) and DOC:DON (**b**) versus PCA axis two. Both relationships were significant ($p < 0.05$)

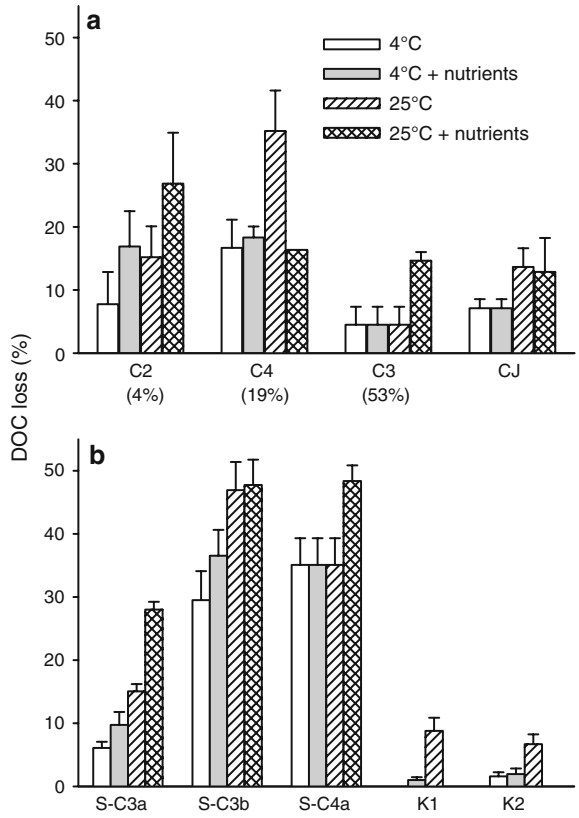

Fig. 8 Proportion of DOC mineralized (±SE) for streams (**a**), and springs and thermokarsts (**b**) after a 40-day incubation. S, denotes a spring followed by the watershed in which the spring was located and K, denotes a thermokarst. Each sample received one of four treatments: 4°C and in situ nutrients, 4°C plus nutrients, room temperature in situ nutrients and room temperature plus nutrients. K1 and K2 treatments without bars were not significantly different than zero

hydrologic conditions, or a combination of all of these factors. South facing watersheds with little permafrost are dominated by hardwood forests of paper birch and quaking aspen, whereas north facing watersheds with extensive permafrost are dominated by black and white spruce. Deciduous litter has higher nitrogen content, lower aromatic carbon content and decomposes faster than coniferous litter (Hobbie et al. 2000; Berg and Meentemeyer 2002; Prescott et al. 2004). Within soil, the cold, wet environment of permafrost dominated watersheds drives reduced plant activity and slower organic matter decomposition rate compared with the drier, warmer soil of watersheds lacking permafrost (Van Cleve et al. 1983; Hobbie et al. 2000). DOM in cold, poorly drained soils have relatively recalcitrant DOM due to long hydrologic residence and substantial time for microbial processing (Wickland et al. 2007). Further, the slow hydrologic transport through high permafrost soils results in greater bulk concentration of DOM compared to lower permafrost, relatively well-drained soils (Wickland et al. 2007). Beyond differences in decomposition, the coniferous vegetation that dominates in high permafrost watersheds has higher aromatic carbon content and higher C:N compared with deciduous vegetation of low permafrost watersheds. These differences in chemistry, coupled with slower decomposition and hydrologic transport likely result in stream water DOM with higher C:N and SUVA in the higher permafrost watershed than in the low and medium permafrost watersheds (Xu et al. 2009).

As hypothesized, the differences in flow paths among watersheds impacted the quality of DOM delivered to CPCRW streams. As water percolates through soil, not only the concentration but also the

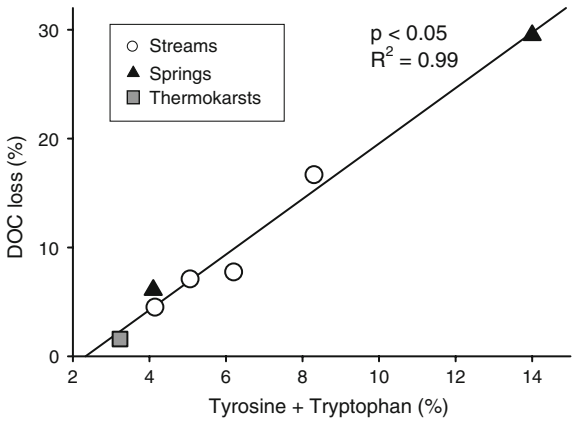

Fig. 9 The proportion of DOC mineralized in bioavailability assays after a 40-day incubation at 4°C and in situ nutrients in stream (*open circles*), spring (*closed triangles*) and thermokarst (*grey squares*) samples versus the proportion of tyrosine (component 9) and tryptophan (component 10) in the fluorescing DOC ($p < 0.05$). Each point is the mean of five replicates samples

composition of DOM changes due to the selective sorption of hydrophobic compounds in the mineral soil leaving hydrophilic compounds in solution (Qualls and Haines 1991; Kaiser and Zech 1998; Ussiri and Johnson 2004). Therefore, the concentration of hydrophobic compounds would be greater in the stream draining the high permafrost watershed than in the streams draining the low and medium permafrost watersheds. These hydrophobic compounds have higher C:N than hydrophilic compounds and contain humic substances that can be highly aromatic (Qualls and Haines 1991; Kaiser et al. 1997; Ussiri and Johnson 2004).

DOM concentration and hydrology

The increase in DOC concentration with discharge in CPCRW streams is similar to patterns observed in headwater catchments in boreal, temperate, desert and alpine regions (Jones et al. 1996; Boyer et al. 1997; Mulholland 1997; Hinton et al. 1998; Buffman et al. 2001; Hood et al. 2006; Petrone et al. 2006, 2007). DOC concentration in the streams draining the low (C2), medium (C4), and high (C3) permafrost watersheds increases with snowmelt and storm flow, with the low permafrost watershed typically having the most rapid response to increased flow, although the total change in discharge and DOC is smaller (Petrone et al. 2006, 2007). In our study, the slope of DOC versus discharge averaged over five summers was greatest in the low permafrost watershed. This quick, short response of DOC during periods of increased flow in the low permafrost watershed may be a result of a smaller contributing area and greater confinement of flow to saturated riparian soils compared to other catchments (Petrone et al. 2007). The riparian zone is flushed more rapidly and frequently of DOC than higher points on the hill slope because of a larger throughput of subsurface water (Boyer et al. 1997).

Although not as significant as differences among watersheds, variation in flow across years resulted in differences in stream chemistry in all streams. In years with smaller and less frequent spates DOC and DON concentrations were lower in all streams, likely due to decreased hydrologic connectivity between the stream and organic soil (Stieglitz et al. 2003; Bolton et al. 2004). During periods of baseflow, the streams draining the low, medium, and high permafrost watersheds are mostly sustained by ground water, which is depleted in DOM relative to soil water (Boyer et al. 1997; Hinton et al. 1998; O'Donnell and Jones 2006). During periods of high flow, the contribution of soil water to stream flow greatly increases, increasing the concentration of DOC and DON in all streams. The pattern of DOC:DON in streams across years was more complicated than that observed for DOC and DON concentrations, with DOC:DON tending to be higher during the high flow years, except for in 2006. Unlike the other relatively high flow years, 2002 and 2003, 2006 was preceded by two unusually low flow years, which may have influenced DOC:DON by altering watershed drainage. The decreased precipitation in 2004 and 2005 may have led to a decrease in soil moisture and an increase in decomposition (Wickland and Neff 2008). As the soil organic matter decomposed, C:N would have declined as carbon was respired leaving DOM with lower C:N to be flushed by the more frequent spates and increased discharge in 2006.

DOM composition and bioavailability

Fluorescent DOM in streams, springs and thermokarsts in CPCRW had high proportions of humic components, low proportions of protein components, and low fluorescence index values (1.3–1.4) consistent with DOM derived from predominantly terrestrial

sources rather than microbially derived DOM. Typically, fluorescent, freshwater DOM is primarily composed of humic substances derived from the breakdown of organic material in water, riparian zones and other soils (McKnight et al. 2001; Katsuyama and Ohte 2002). However, the protein fraction of DOM in freshwaters can be significant as a result of increases in anthropogenic inputs, urbanization (Baker and Spencer 2004), glacial inputs (Battin et al. 2004, Lafreniére and Sharp 2004), decreases in flow from organic soil (Mladenov et al. 2005; Hood et al. 2006), and are due to increased primary productivity (Lu et al. 2003). Terrestrially derived DOM typically has a high aromatic carbon content and higher C:N reflecting the presence of tannin-like and humic-like substances originating from higher plants and soil organic matter (Battin 1998). Fluorescence index values of terrestrially derived DOM in streams range from 1.2 to 1.5 (McKnight et al. 2001; Mladenov et al. 2005; Hood et al. 2006), however leaf litter leachates from some boreal forest plants have been shown to have FI values greater than 1.5 (Wickland et al. 2007). While freshly leached DOM from plant litter could be an important component of DOM in this study, after a day or two of light exposure, such high FI values of leaf litter leachates will decrease to typical FI values of terrestrially derived DOM (Jaffé et al. 2004). In contrast to higher plant/terrestrial DOM sources, lakes and rivers dominated by microbially derived DOM typically have FI values ranging from 1.6 to 2.0 (McKnight et al. 2001; Baker and Spencer 2004; Battin et al. 2004; Lafreniére and Sharp 2004).

The PCA analysis of DOM fluorescence revealed distinct groups among streams, springs, and thermokarsts supporting our hypothesis that hydrologic flow path influences the chemical composition of DOM. Factor 1 was associated with an increase in component eight and a decrease in component two, and is likely controlled by diagenetic processing (photodegradation). Based on the fluorescence spectrum, component two may represent an oxidized quinone, whereas component eight is a reduced version of the quinone (Cory and McKnight 2005). Thermokarst samples formed a distinct group along the PCA one axis. Surprisingly, even with often anoxic conditions (based on increased methane concentration relative to streams and springs; Jones, unpublished data), thermokarst samples contained a higher proportion of the oxidized quinone than streams and springs. The enhanced presence of component two in thermokarst DOM is most likely controlled by photochemical exposure and processing of DOM. Photodegradation can change the structure (Waiser and Robarts 2004) and fluorescence properties (Moran et al. 2000) of DOM. In fact, during photodegradation studies of DOM, a component with spectral characteristics similar to component two was reported to increase in abundance at the expense of the other DOM components (Stedmon et al. 2007). The extent of DOM photodegradation may be greater in thermokarsts than in springs and streams due to shallower water, greater terrestrial input of DOC, and a higher incidence of irradiation (Waiser and Robarts 2004). The presence of an oxidized quinone-type component in thermokarst samples may also be attributable to the heterogeneous structure of thermokarsts and anaerobic respiration. Thermokarsts are heterogeneous in structure and likely have a complex matrix of oxidized and reduced regions, which may favor the oxidation of reduced quinones produced in anoxic environments. Additionally, reduced humics and other extracellular quinones have been shown to donate electrons for the microbial reduction of electron acceptors during anaerobic respiration (Lovely et al. 1999).

The separation of samples based on PCA factor 2 was likely related with DOM source. Components 9 and 10 (tyrosine and tryptophan) are protein-like components most likely of microbial origin, whereas component one is a terrestrial humic-like component (Coble et al. 1998). Spring S-C3b formed a distinct group along based on PCA factor 2. Spring S-C3b had a high electrical conductance, associated with deeper groundwater flow and long groundwater residence time (White et al. 2008), and a low DOC:DON, associated with a high percentage of proteinaceous carbon. Thus, S-C3b likely represents a deeper groundwater spring with increased microbial production relative to streams and thermokarsts. This increased microbial production may be due to increased ground water residence time allowing microbial populations to increase, higher quality organic matter due to processing and selective adsorption in the mineral soils, or simply lower inputs of terrestrial humic-like components.

The proportion of DOC mineralized in bioavailability assays from CPCRW streams, springs and thermokarsts (2–35%) is similar to the percent of DOC

mineralized in samples from streams along a gradient from discontinuous to continuous permafrost (5–28%; Kawahigashi et al. 2004), and in temperate (16.5–34.4%, Volk et al. 1997; 7–15%, Sobczak and Findlay 2002) and tropical (22%; Kim et al. 2006) regions. Bioavailability of DOM in CPCRW streams was intermediate between springs and thermokarsts, indicating multiple sources contribute to DOM in streams. The higher conductivity due to weathering, higher proportion of proteinaceous carbon due to increased microbial primary production, and greater proportion of DOC lost in springs S-C3b and S-C4a suggest that deeper groundwater flows are a source of relatively bioavailable DOM to streams in CPCRW. In contrast, thermokarsts have high concentrations of relatively unavailable DOC and are a source of recalcitrant DOM to streams. The difference in DOC bioavailability among streams, springs, and thermokarsts are most likely due to differences in DOC residence time, extent of prior microbial processing, and DOC chemistry (Wickland et al. 2007). The absolute concentration of bioavailable DOM did not vary among CPCRW streams, springs, and thermokarsts indicating that the lower proportions of bioavailable DOM in streams and thermokarsts were compensated for by higher overall DOM concentration.

The proportion of tyrosine and tryptophan was highly correlated with the proportion of DOC mineralized in bioavailability assays from CPCRW samples. Amino acid/protein carbon has been shown to be an excellent indicator of bioavailability of DOM (Amon et al. 2001; Cammack et al. 2004) and is thought to be diagenetically young DOM with high energy content (Amon et al. 2001). The small proportion of proteinaceous carbon in streams, springs and thermokarsts suggests that most of the DOM exported from soils in CPCRW may not be readily used for microbial respiration/production along the stream reach and is probably transported unaltered downstream.

DOM and climate change

DOM input to streams will likely decrease with the degradation of permafrost in CPCRW based on differences in DOM concentration and composition in streams draining watersheds differing in permafrost coverage. Changes may include a declines in DOC and DON concentrations, DOC:DON and SUVA, possibly accompanied by an increase in the amount of bioavailable DOM in streams if the contribution of deeper groundwater flow to streams increases. Interestingly, the absolute concentration of bioavailable DOM may not substantially change in spite of the increased proportion of bioavailable DOM because the concentration of DOM in deeper ground water is lower than in shallower, soil flow paths. Moreover, superimposed on changing watershed flow paths is the input of DOM from thermokarst formation. Thermokarst formation will likely increase with permafrost thaw and accordingly, if thermokarsts are hydrologically connected to streams, the contribution of recalcitrant DOM to streams will likely increase.

Within the greater boreal forest of interior Alaska, riverine DOM fluxes will respond to both hydrologic and biologic responses to climate change. The CPCRW is within the Yukon River drainage; the Yukon River receives from upland streams and rivers similar to the streams of CPCRW and glacially fed rivers. The DOC concentration in CPCRW streams is similar to other upland streams such as the Chena River (4.5 mg/L, Cai et al. 2008), but is higher than the glacially fed Tanana River (2.6 mg/L, Striegl et al. 2007), and the upper Yukon River (2.9 mg/L, Guo et al. 2007), which receives a mixture of flows from upland and glacial streams. The export of DOC from the greater lower Yukon River will undergo a myriad of changes as glaciers melt and contribute increased flow but then ultimately retreat and disappear, and while permafrost thaws and watershed flowpaths through upland catchments change from flowing through organic soil to deeper mineral and bedrock regions. Coupled to these changes in the sources of DOC and the associated changes in DOM chemical composition, in-river processing will also likely change. The C:N of DOM in the headwater streams of CPCRW is lower than in the higher order branches of the Yukon River (Chena River = 41, Cai et al. 2008; Tanana = 31, Dornblaser and Striegl 2007; Yukon River = 36, Dornblaser and Striegl 2007). These increases in the C:N of DOM indicate a decline in the bioavailability of DOM in higher-order reaches of the Yukon River, but that the degree of processing may vary among drainage types.

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