

Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds

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Abstract The composition and biodegradability of streamwater dissolved organic matter (DOM) varies with source material and degree of transformation. We combined PARAFAC modeling of fluorescence excitation-emission spectroscopy and biodegradable dissolved organic carbon (BDOC) incubations to investigate seasonal changes in the lability of DOM along a soil-stream continuum in three soil types: bog, forested wetland and upland forest. The percent BDOC ranged from 7 to 38% across all sites, and was significantly greater in soil compared to streamwater in the bog and forested wetland, but not in the upland forest. The percent BDOC also varied significantly over the entire sampling period in soil and streamwater for the bog and forested wetland, as BDOC peaked during the spring runoff and was lowest

during the summer months. Moreover, the chemical quality of DOM in wetland soil and streamwater was similar during the spring runoff and fall wet season, as demonstrated by the similar contribution of protein-like fluorescence (sum of tyrosine and tryptophan fluorescence) in soil water and in streams. These findings suggest that the tight coupling between terrestrial and aquatic ecosystems is responsible for the delivery of labile DOM from wetland soils to streams. The contribution of protein-like fluorescence was significantly correlated with BDOC ($p < 0.001$) over the entire sampling period indicating DOM is an important source of C and N for heterotrophic microbes. Taken together, our findings suggest that the production of protein-rich, labile DOM and subsequent loss in stream runoff might be an important loss of labile C and N from coastal temperate watersheds.

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Introduction

Dissolved organic matter (DOM) is ubiquitous in the environment and consists of a wide array of compounds and functional groups. DOM is important in many freshwater ecosystems as a source of carbon and energy, but also because of its acid base characteristics,

affinity for metals, and control on the depth of the photic zone (see Aitkenhead-Peterson et al. 2003). The character of aquatic DOM varies according to precursor material, which falls broadly into allochthonous (terrestrially-derived) and autochthonous (derived from within the aquatic ecosystem) source pools. Terrestrial contributions of plant and soil organic matter are the primary source of carbon to temperate headwater streams, although in-stream carbon contributions and carbon transport from upstream sources can become more important as stream order increases (Vannote et al. 1980).

The concentration and chemical quality of DOM transported from terrestrial to aquatic ecosystems is an important indicator of watershed-scale biogeochemical processes (Hood et al. 2005), and controls on DOM concentrations in soils (Neff and Asner 2001) and streams (Mulholland 2003) are well-studied. As allochthonous DOM moves along the soil-stream continuum from its source in the soils to the watershed outlet, the concentration and composition of DOM reflects both source material (McDowell and Likens 1988) and distance downstream along the continuum (Dawson et al. 2001). DOM composition is influenced by biological transformations (Kaplan and Bott 1983) and abiotic sorption in the soil (McDowell and Likens 1988) and in the stream (McDowell 1985). The extent to which DOM is altered with passage through the watershed varies with seasonal changes in biotic demand (Fenner et al. 2005) and dominant hydrologic flowpaths (Schiff et al. 1997). For example, biodegradable dissolved organic carbon (BDOC) from three rivers draining into the Arctic Ocean was greatest during the spring freshet and lowest during the summer (Holmes et al. 2008). This temporal pattern in BDOC was attributed to reduced biotic demand combined with DOM transport via shallow soil flowpaths. Therefore, knowledge of how BDOC varies temporally and spatially along the soil-stream continuum is critical in understanding DOM cycling in watersheds.

Wetlands are an important source of DOM to aquatic ecosystems (Agren et al. 2007) and DOM quality and biodegradability varies seasonally and by wetland type (Fellman et al. 2008). Northern wetlands are of particular interest because they contain approximately one-third of the world's soil carbon (Gorham 1991). Despite abundant research on DOM export in northern watersheds (e.g. Holmes et al.

2008), little attention has been given to the carbon rich, mesic to wet environments of southeast Alaska. Approximately 29% of the land area in southeast Alaska is wetland, and 15% of this wetland is peatland (Cowardin et al. 1979). Therefore, the well-defined watersheds of southeast Alaska that include well-drained, mineral soils interspersed with saturated, peatland soils present an excellent opportunity to develop a process-level understanding of the linkages between terrestrial ecosystems and stream biogeochemistry.

The connectivity of carbon cycling in peatland-stream ecosystems has been investigated by determining the major sources and sinks of aquatic carbon within watersheds (Dawson et al. 2004) and by comparing downstream changes in dissolved organic carbon (DOC) concentrations with spatial changes in soil carbon pools (Billet et al. 2006). Despite this attention to carbon export from wetlands, few integrated studies at the watershed scale have developed an understanding of how wetlands influence the chemical quality and biodegradability of DOM along a soil-stream continuum. In this study, we combined PARAFAC modeling of fluorescence excitation-emission spectroscopy, specific UV absorbance (SUVA₂₅₄) of DOC and BDOC incubations to evaluate seasonal changes in the chemical quality and lability of DOM along a soil-stream continuum in three common soil types (bog, forested wetland and upland forest) in southeast Alaska. Here we refer to the soil-stream continuum as the movement of DOM from its source in the soil water to the sub-catchment outlet streams. We hypothesized that BDOC in streams would be higher during the spring snowmelt and fall wet season compared to the summer growing season, due to the interaction between BDOC production/removal processes and seasonal changes in soil hydrology.

Methods

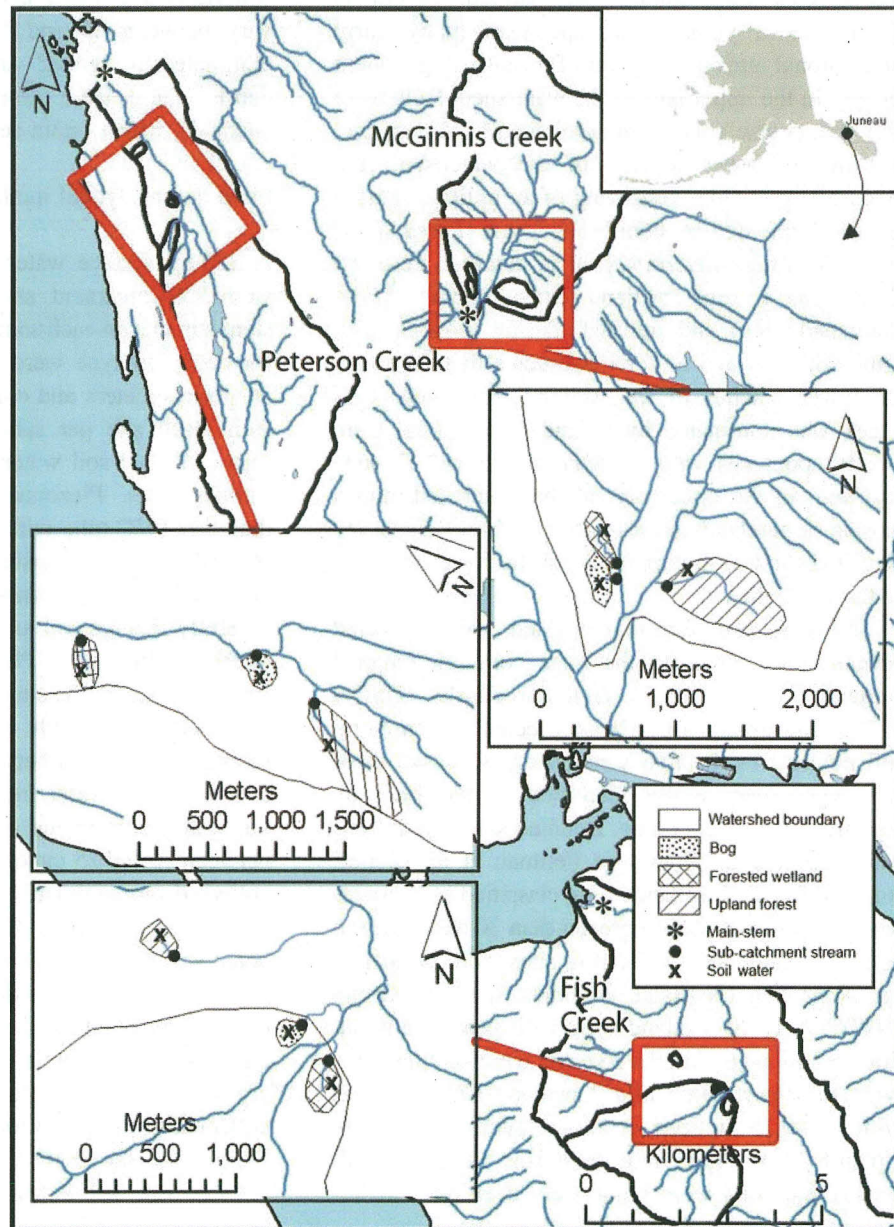
Site descriptions and experimental design

Soil and streamwater were collected within three coastal temperate rainforest watersheds, located near Juneau, Alaska. Juneau has a cool, maritime climate with a mean annual temperature of 4.7°C and a mean annual precipitation of 1,400 mm at sea level, most of which falls in the autumn as rain or as snow at

upper elevations during the winter. Seasonal precipitation and long summer days produce three watershed hydrological regimes during the main runoff season: (1) spring snowmelt (May), (2) summer draw down (June–early August) and (3) fall wet season (early August–November). After spring snowmelt occurs; evapotranspiration and lower precipitation result in a period of soil water table drawdown, typically in June or July, during which streamflow decreases. Streamflow in the region then peaks during the autumn rainy season.

We established three sub-catchments within each of the three forested watersheds in the spring of 2006. Each of the three sub-catchments represents a distinct soil type: bog, forested wetland and upland forest. Within each watershed, we sampled weekly at three locations along the soil–stream continuum from May through October: (1) soil water from each soil type, (2) sub-catchment outlet streams and (3) watershed main-stem streams (Fig. 1). This experimental design resulted in 9 soil water (3 soil types $\times$ 3 reps), 9 sub-catchment stream (3 soil types $\times$ 3 reps) and 3 main-

Fig. 1 Map of Alaska and experimental design. Samples were collected weekly from soil water, sub-catchment outlet stream and main-stem streams for the three watersheds from May through October



stem stream samples collected on each sample date (26 sample dates). The May through October sampling period was the approximate length of the snow free season.

The three study watersheds (Fish, McGinnis and Peterson Creeks) represent different combinations of wetland coverage, glacial recession, dominant vegetation and valley morphology. All three watershed main-stem streams receive anadromous salmon runs throughout the summer and early autumn (June through September), although the spawning density and species vary among each stream. McGinnis Creek was a young landscape with many early successional attributes typical of recently deglaciated terrain. In the upper part of the watershed, soils were thin with sparse vegetation dominated by *Alnus* spp., and in the lower reaches of the watershed, the landscape was older consisting of an uplifted marine terrace dominated by coniferous forest (*Picea sitchensis* and *Tsuga heterophylla*). In contrast, Peterson Creek has a high wetland extent (53% of the watershed area) and uplifted marine terraces with some colluvial and alluvial sediments that dominate the lower reaches of the wetland watershed. Fish Creek was dominated by upland forest (soils were mostly spodosols with *T. heterophylla* and *T. mertensiana*) in the upper part of the watershed, and a mosaic of peatlands mixed with coniferous forest (*P. sitchensis* and *T. heterophylla*) in the lower portions of the watershed.

The bog and forested wetland were selected because they represent the most common mapped wetland communities in southeast Alaska (USDA 1997). The upland forest was selected as a mineral soil contrast to the two wetland types. These three soil types were easily identified in the field by topography and vegetation. Detailed soil descriptions were reported previously in Fellman et al. (2008). Bog and forested wetlands were classified as histosols with C:N ratios typically greater than 30 and a carbon content greater than 35%. Bog sites were typical of the slope bog (National Wetlands Working Group (NWWG) 1988) wetland type with peat accumulations >2 m deep, and the forested wetland sites were typical of the raised peatland swamp (NWWG 1988) with 0.5–0.75 m deep peat overlaying glacial till. Upland forest sites were spodosols (Typic Humicryod) and soils were moderately deep and moderately well-drained, due to their steep slopes.

The three soil types were common landscape features in the steeply sloping watersheds of southeast Alaska. The hydrologic flow systems in this complex terrain can be characterized by a combination of surface, near surface and deeper groundwater flow paths, and changes in slope or subsurface geometry that interrupt hillslope flow paths can result in the occurrence of headwater wetlands (see Fitzgerald et al. 2003). The small, headwater streams draining the three soil types have channels that were characterized by a sequence of riffles or small waterfalls and small pools. Stream channel widths vary between 25 and 50 cm and sediments were dominated by gravel and small pebbles. Organic debris dams were common features within the channels, which retain sediment and woody debris.

Field and analytical methods

A 250 ml surface water grab sample was collected from sub-catchment streams and watershed main-stem streams on each sample date. Soil water samples for each soil type were collected from four, 25 cm deep piezometers and combined to yield one sample from each site per sample date (3 soil types x 3 reps = 9 total soil water samples collected for each sample date). Piezometers consisted of a 3.1 cm diameter PVC tube with slits (2 mm) sawn between 20 and 25 cm. To install each piezometer, a hand auger of a slightly smaller diameter was used to carefully remove soil and the piezometer was placed in the resulting hole. Piezometers were inserted in a small grid across the sites and routine sampling began following a 1 month equilibration period. Tygon tubing attached to a battery-operated pump was used to sample soil water from the piezometers. Because the water table in the wetland sites was commonly between 10 and 25 cm of the soil surface, piezometers collected predominantly groundwater from the saturated zone throughout the sampling period. However, here we refer to the water collected from the piezometers as soil water. The 25 cm piezometer depth corresponds to the approximate acrotelm (typically aerobic)/catotelm (typically anaerobic) boundary in bog and forested wetland sites. Soil water collected from upland forest sites was a composite of DOM from the O (0–15 cm) and upper B horizons (15–25 cm). All water samples were field-filtered through pre-combusted, glass fiber filters (nominal

pore size 0.7 μm) and stored in the refrigerator until analysis within 72 h of collection.

Soil and streamwater DOC (determined by non-purgeable organic carbon analysis) and total dissolved N (TDN) concentrations were analyzed via high temperature combustion on a Shimadzu TOC/TN-V analyzer. Analytical precision for DOC during the measurement period ranged from 0.02 to 0.04 mg C l^{-1} (mean standard deviation for identical samples re-analyzed during analytical runs) for DOC concentrations less than 5 mg C l^{-1} and 0.1–0.4 mg C l^{-1} for samples greater than 5 mg C l^{-1} . Ion chromatography (Dionex ICS-1500 and 2500) was used to measure $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$. Because nitrite concentrations were typically below detection (5–8 $\mu\text{g N l}^{-1}$), dissolved organic N (DON) was calculated as the difference between TDN and dissolved inorganic N ($\text{DIN} = \text{NH}_4\text{-N} + \text{NO}_3\text{-N}$). Soluble reactive phosphorus (SRP) was measured using the ascorbic acid method (Murphy and Riley 1962), total dissolved phosphorus (TDP) was measured using a persulfate digestion (Valderrama 1981), and dissolved organic phosphorus (DOP) was calculated as the difference between TDP and SRP.

Biodegradable DOC (BDOC) was calculated as the difference in DOC before and after a 30 day laboratory incubation following the methods of Fellman et al. (2008). Briefly, water samples were initially filtered through a 0.2 μm filter, a bacterial inoculum was added, and samples were incubated at 25°C for 30 days in the dark. After 30 days, the solution was re-filtered through a 0.2 μm filter, DOC was re-measured (we measured initial and final DOC only), and BDOC was calculated as the difference in sample DOC before and after the 30 day incubation. If necessary, samples were diluted to approximately 15 mg C l^{-1} to prevent excessive microbial growth. The bacterial inoculum (prepared fresh before each incubation) was prepared by leaching soil collected in the riparian zone from a combination of the sites (soil was combined to form a composite), diluted 1:1 with deionized water and incubated at 25°C for 24 h before addition to the sample solution.

Spectroscopic analyses and PARAFAC modeling

The specific UV absorbance of DOC (SUVA_{254}), which is an indicator of aromatic C content, was measured on soil and stream water samples following

the procedures of Weishaar et al. (2003). Fluorescence excitation–emission matrices (EEM) of DOM were measured on a Fluoromax-3 (Jobin Yvon Horiba) fluorometer with a xenon lamp following the procedures of Hood et al. (2007). Water samples were diluted with Milli-Q water to an optical density of 0.02 at 300 nm in order to avoid inner filter effects (Green and Blough 1994). EEMs were corrected for instrument bias and Raman normalized using the area under the water Raman peak at excitation 350 nm.

Fluorescence EEMs were analyzed using the multivariate modeling technique parallel factor analysis (PARAFAC). Fluorescent DOM is a subfraction of bulk DOM and we currently cannot assess the contribution fluorescence makes to the total DOM pool. However, studies have shown that PARAFAC components (the exact compounds responsible for the fluorescence of these groups are still unknown) are useful for tracing the dynamics of DOM in natural ecosystems (Stedmon et al. 2003; Cory and McKnight 2005). PARAFAC modeling of EEMs was conducted with MATLAB using the PLS_toolbox version 3.7 (Eigenvector Research Inc. 2006) following the procedures of Stedmon et al. (2003). The appropriate number of modeled components was determined using core consistency diagnostics (Ohno and Bro 2006) followed by a split-half validation (Stedmon et al. 2003). If the correct number of fluorescent components is selected using the PARAFAC model, the components can be compared for each sample by determining the relative contribution of each component to the total DOM fluorescence. This was determined by quantifying the contribution of each component and dividing that by the total fluorescence of all the modeled PARAFAC components.

Our PARAFAC model identified a total of nine unique components within the fluorescence EEMs (Table 1). All nine components identified by our model have been previously identified as either part of a PARAFAC model or through peak picking (visual inspection of the EEMs to locate fluorophores) of fluorescence EEMs. Even though our PARAFAC model identified nine components, we focused our analysis on five of the components: 1 (humic-like), 4 (fulvic-like), 6 (humic-like), 8 (tryptophan-like) and 9 (tyrosine-like). These components were selected because they explained a large amount of the variability in the data set and were useful in elucidating differences in the chemical quality of DOM in our

Table 1 Characteristics of the nine different components identified by the PARAFAC model in this study

Comp.	Ex/Em maxima (nm)	Components identified from previous studies	Description
1	<250/450–460	Stedmon and Markager (2005) Component 1	Humic-like fluorophore
2	330/460–480	Cory and McKnight (2005) Component 1	Humic-like fluorophore
3	290/510	Cory and McKnight (2005) Component 5 (Q2)	Semi-quinone-like fluorophore
4	340/410–420	Baker (2001) Component B	Fulvic-like fluorophore
5	<250/414	Stedmon and Markager (2005) Component 3	Humic-like fluorophore
6	295/414	Coble (1996) Component M	Humic-like fluorophore
7	<250/400	Stedmon and Markager (2005) Component 6	Humic-like fluorophore
8	280/330–340	Stedmon and Markager (2005) Component 7	Tryptophan-like fluorophore
9	275/304–306	Stedmon and Markager (2005) Component 8	Tyrosine-like fluorophore

watersheds. Additionally, DOM is a complex mixture of organic compounds and it is likely that each component represents a group of fluorophores with similar fluorescence characteristics. For example, tyrosine fluorescence is likely a mixture of proteinaceous compounds with similar fluorescence characteristics, thus, we refer to tyrosine fluorescence as "tyrosine-like."

Statistical analyses

Temporal differences in each parameter across the three soil types were examined using a mixed-model, repeated measures analysis of variance (ANOVA) with a compound symmetry covariance structure. The sub-catchments/soil types nested within the larger watershed were considered treatments and the watersheds as blocks. All values for different sample dates were considered repeated measurements. This statistical design had an $N = 3$ for the soil type comparison, and an $N = 26$ for the temporal analysis, where each " N " was the mean of the three replicate sites on that date. ANOVA was performed using Proc Mixed (SAS Institute Inc. 2003) and were statistically significant at $p < 0.05$. Linear regression models using Proc GLM (SAS Institute 2003) were used to

evaluate relationships between PARAFAC components, dissolved nutrient concentrations and BDOC.

Results

Dissolved nutrient concentrations

Average DOC concentrations varied >10x across the soils and streams sampled and ranged from 1.4 to 33.1 mg C l⁻¹, whereas average DON concentrations ranged from 0.1 to 0.9 mg N l⁻¹ across the study sites (Table 2). DON accounted for 80% or more of TDN for both soil and stream water for all sample dates, except for the McGinnis Creek main-stem in which DON was only about 50% of TDN. DOP was the dominant fraction of TDP for all sites and ranged from 5.8 to 44.7 µg P l⁻¹.

Average dissolved C, N, and P concentrations were greatest in soil water for all soil types and were lower in sub-catchment outlet streams (Table 2). Average DOC concentration decreased from soils to sub-catchment streamwater by 33% in the bog, 44% in the forested wetland and 66% in the upland forest. Average concentrations of N and P decreased by over 55% along the soil-stream continuum in the three soil

Table 2 Mean (± 1 SE) and median of soil and streamwater dissolved nutrient concentrations for all 26 sample dates

	DOC mg C l ⁻¹	TDN mg N l ⁻¹	DON mg N l ⁻¹	TDP μg P l ⁻¹	DOP μg P l ⁻¹
Sub-catchment soils					
Bog	26.1 (3.9) 25.4	0.9 (0.1) 0.8	0.9 (0.1) 0.7	48.4 (7.4) 35.5	31.9 (4.1) 17.7
Forested wetland	33.1 (3.5) 32.9	0.8 (0.1) 0.7	0.8 (0.1) 0.7	64.8 (5.9) 44.6	44.7 (6.9) 28.9
Upland forest	15.2 (2.1) 9.8	0.6 (0.1) 0.5	0.5 (0.1) 0.3	46.4 (5.0) 36.7	32.6 (4.1) 21.2
Sub-catchment streams					
Bog	17.5 (1.8) 17.1	0.4 (0.1) 0.4	0.4 (0.1) 0.4	14.1 (2.6) 13.1	10.2 (2.1) 9.5
Forested wetland	18.7 (4.8) 18.1	0.3 (0.1) 0.3	0.3 (0.1) 0.3	14.8 (2.8) 12.9	11.0 (2.5) 9.6
Upland forest	5.5 (1.8) 4.8	0.2 (0.1) 0.1	0.2 (0.1) 0.1	9.1 (1.4) 8.0	7.0 (1.1) 5.8
Main-stem streams					
Peterson creek	8.4 (0.5) 8.3	0.5 (0.1) 0.4	0.4 (0.1) 0.3	24.3 (5.9) 23.5	16.2 (1.8) 12.3
McGinnis creek	1.4 (0.3) 0.8	0.2 (0.1) 0.1	0.1 (0.1) 0.1	8.9 (0.6) 8.2	5.8 (0.7) 5.6
Fish creek	5.0 (0.5) 4.6	0.2 (0.1) 0.1	0.2 (0.1) 0.1	8.7 (2.1) 7.7	6.5 (1.2) 5.6

Soil water was collected from 25 cm piezometers located within each sub-catchment

types. There was little change in the fraction of TDN as DON moved from soils to sub-catchment streams in the three soil types; however, the fraction of TDP as DOP increased from 68% in soil water to 75% in sub-catchment outlet streams. A comparison of the watershed main-stem streams showed that average dissolved C, N and P concentrations in the McGinnis and Fish Creek main-stems were equal to or lower than concentrations in sub-catchment streams and soil waters. However, average N and P concentrations in the Peterson Creek main-stem were greater than in sub-catchment streams, due to the presence of anadromous salmon that have been shown to significantly increase N and P concentrations during late summer spawning in Peterson Creek (Hood et al. 2007).

Biodegradable DOC

BDOC concentrations were significantly greater in soil water than stream water for all three soil types ($p < 0.05$, Table 3). Soil and streamwater BDOC concentrations were significantly greater in the bog and forested wetland than in the upland forest ($p < 0.05$), but soil and stream water BDOC concentrations did not differ between the bog and forested wetland ($p > 0.05$). Similar to the pattern in concentrations of BDOC, the percent BDOC was significantly greater in soil water compared to streamwater in the bog ($p = 0.03$) and forested wetland

($p = 0.01$) over the entire sampling period (Table 3). The percent BDOC varied significantly over the entire sampling period in soil water ($p < 0.005$) and streams ($p < 0.001$) for the bog and forested wetland, as BDOC peaked during the spring runoff (May) and was lowest during summer (June through August) in both soil and streamwater (Fig. 2a-b). However, percent BDOC was similar in soil and stream water for a brief period during the spring runoff and fall.

The percent BDOC in the upland forest did not vary significantly over the entire sampling period in streamwater ($p = 0.07$) and soil water ($p = 0.09$, Fig. 2c). There was no significant difference for the upland forest in percent BDOC between soil and stream water for the entire sampling period ($p > 0.5$, Table 3). Comparing the three soil types showed that percent BDOC was significantly greater in the upland forest stream compared to the bog ($p = 0.002$) and forested wetland ($p < 0.001$) streams, while streamwater BDOC in the bog was significantly greater than the forested wetland ($p = 0.02$, Table 3). Soil water percent BDOC was significantly greater in the bog compared to the upland forest ($p = 0.04$) and forested wetland ($p = 0.01$).

In the watershed main-stem streams, the percent BDOC was greater in the McGinnis Creek main-stem compared to Fish and Peterson Creek throughout the sampling period (Fig. 3a). However, concentrations of BDOC in the Peterson Creek main-stem were on average more than twice as high as those in McGinnis

Table 3 Mean (± 1 SE) for BDOC, SUVA₂₅₄ of DOC and the relative contribution of the PARAFAC components discussed in this study

Site	BDOC mg C l ⁻¹	BDOC % C loss	SUVA ₂₅₄ l mg-C ⁻¹ m ⁻¹	Protein-like %	Humic-like Comp. 1 (%)	Fulvic-like Comp. 4 (%)	Humic-like Comp. 6 (%)
Sub-catchment soils							
Bog	7.3 (0.7) ^a	25.8 (2.5) ^b	4.1 (0.1) ^a	11.4 (0.7) ^b	34.1 (0.8) ^b	0.4 (0.1) ^b	3.5 (0.1) ^a
Forested wetland	8.1 (0.6) ^a	19.4 (3.6) ^a	4.4 (0.1) ^b	7.1 (0.4) ^a	28.4 (0.6) ^a	10.1 (0.4) ^a	5.0 (0.1) ^b
Upland forest	5.4 (0.5) ^b	21.7 (1.8) ^a	4.1 (0.1) ^a	8.1 (0.9) ^a	27.2 (0.3) ^a	9.6 (0.4) ^a	5.8 (0.1) ^c
Sub-catchment streams							
Bog	3.2 (0.3) ^a	17.5 (1.9) ^a	4.3 (0.1) ^a	5.5 (0.5) ^a	33.2 (0.6) ^b	0.9 (0.1) ^b	2.8 (0.1) ^a
Forested wetland	3.1 (0.5) ^a	12.6 (2.6) ^b	4.5 (0.1) ^a	3.5 (0.5) ^b	23.4 (0.9) ^a	13.2 (0.8) ^a	3.8 (0.1) ^b
Upland forest	1.4 (0.2) ^b	22.9 (2.1) ^c	3.5 (0.4) ^b	5.6 (0.6) ^a	21.3 (0.6) ^a	15.6 (0.7) ^a	4.5 (0.1) ^c
Main-stem streams							
Peterson creek	1.7 (0.3)	16.1 (2.7)	4.3 (0.2)	2.8 (0.8)	31.3 (0.3)	3.2 (0.1)	2.1 (0.1)
McGinnis creek	0.6 (0.1)	30.1 (1.4)	2.5 (0.1)	5.6 (0.4)	18.7 (0.2)	12.6 (0.3)	3.3 (0.1)
Fish creek	1.2 (0.1)	19.8 (1.6)	3.9 (0.2)	2.0 (0.4)	29.3 (0.4)	4.8 (0.2)	1.8 (0.2)

Protein-like fluorescence is the sum of tyrosine and tryptophan-like PARAFAC components

The mean for PARAFAC components and SUVA₂₅₄ values was generated from all 26 samples dates. However, BDOC values were determined from incubations for 12 different sample dates

Different superscript letters denote significant differences between soil types at $p < 0.05$ using a repeated measures analysis of variance and $N = 3$

Creek (Fig. 3b). There was no strong temporal pattern in percent BDOC in the McGinnis Creek main-stem as streamwater BDOC was greater than 20% throughout the sampling period. In contrast, percent BDOC in Peterson Creek was high during the spring, decreased to a low of 8–10% during June and July, exhibited maxima during the three week period when spawning salmon were present in the stream and returned to near spring levels of approximately 15–20% during the fall.

Spectroscopic properties of DOM and PARAFAC modeling

The humic-like component 1 was the dominant PARAFAC component in soil and streamwater DOM samples collected for the three soil types (Table 3). The contribution of humic-like fluorescence was significantly greater in soil than streamwater in the forested wetland ($p = 0.02$) and upland forest ($p = 0.008$), but not the bog ($p > 0.5$). Humic-like fluorescence in both soil and streamwater was significantly greater in the bog compared to the forested wetland and upland forest ($p < 0.001$). The fulvic-like component 4 was significantly greater in

streamwater than soil water for all soil types ($p < 0.05$), and was significantly greater in the forested wetland and upland forest compared to the bog for both soil and stream water ($p < 0.001$, Table 3). The humic-like component 6, which may be an indicator of diagenetically young DOM (Burdige et al. 2004), was significantly greater in soil compared to stream water in all soil types ($p < 0.05$, Table 3).

Similar to the temporal pattern observed in BDOC along the soil-stream continuum, the relative contribution of protein-like fluorescence (sum of tyrosine and tryptophan-like fluorescent components) varied significantly over the entire sampling period in soil water ($p < 0.05$) and streams ($p < 0.01$) for all three soil types, as protein-like fluorescence peaked during the spring runoff and was lowest during the summer months in both soil water and streams (Fig. 4a–c). The contribution of protein-like fluorescence was significantly greater in soil water than in streamwater for all three soil types ($p < 0.04$). However, protein-like fluorescence was similar in soil and streamwater for a brief period during the spring runoff and fall for the three soil types. Comparing the three soil types showed that soil and stream water protein-like

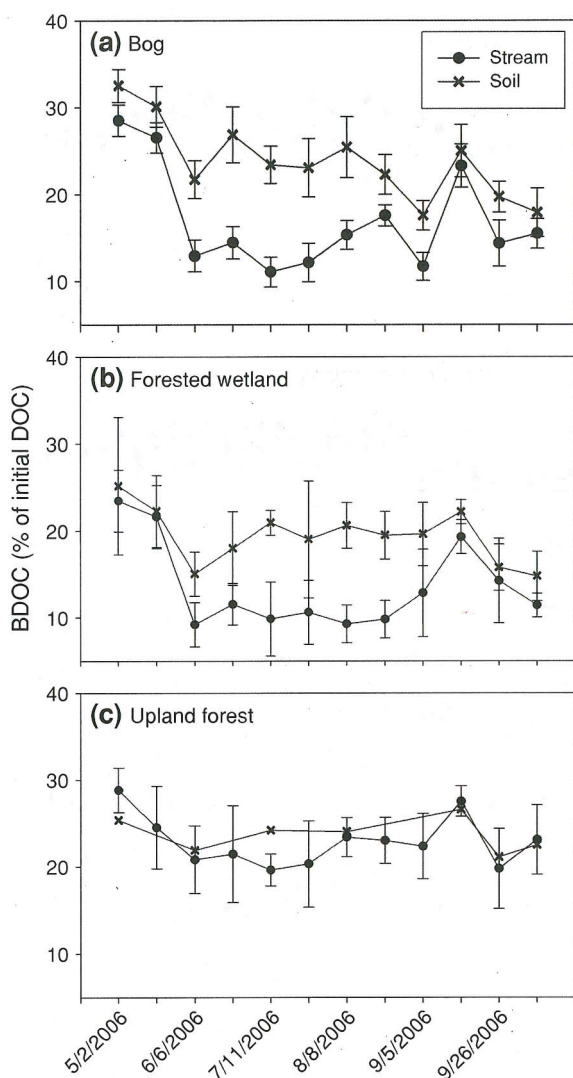


Fig. 2 Time series of BDOC for soil water and streamwater in the **a** bog, **b** forested wetland and **c** upland forest during the May through October sampling season. Error bars indicate ± 1 SE and $N = 3$ for each sample date. SE bars are not present for soil water in the upland forest because soil water was frequently unavailable to collect at all three sites

fluorescence were significantly greater in the bog than the forested wetland ($p = 0.04$ for both comparisons), although soil water ($p = 0.01$) but not streamwater ($p = 0.1$) protein-like fluorescence was significantly greater in the bog than in the upland forest (Table 3).

The $SUVA_{254}$ of DOC (indicator of aromatic C content) varied significantly over the entire sampling period in soil water ($p < 0.05$) and streams ($p < 0.05$) for the bog and forested wetland, as

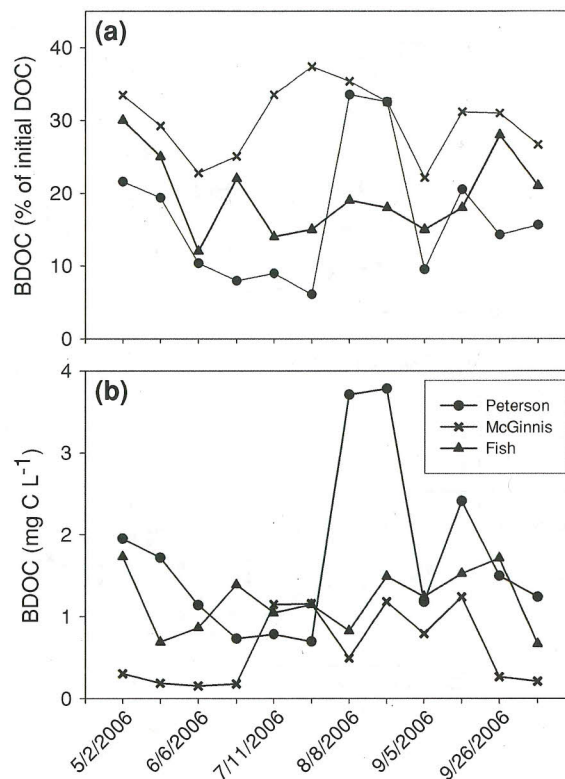


Fig. 3 Time series of **a** percent BDOC and **b** concentrations of BDOC in the three watershed main-stems during the May through October sampling season

$SUVA_{254}$ values were lowest during the spring runoff and greatest during the summer months (Fig. 5a–b). There was no significant difference in $SUVA_{254}$ values between soil and streamwater for the bog ($p = 0.1$) and forested wetland ($p = 0.2$, Table 3). In the upland forest, $SUVA_{254}$ varied significantly over the entire sampling period in streamwater ($p < 0.001$), but not soil water ($p = 0.2$), as streamwater $SUVA_{254}$ values were lowest during the summer months (Fig. 5c). The $SUVA_{254}$ values in the upland forest were significantly less in streamwater compared to soil water ($p = 0.05$). In addition, streamwater $SUVA_{254}$ values were significantly less in the upland forest compared to those in the bog ($p = 0.03$) and forested wetland ($p = 0.02$, Table 3).

Protein-like fluorescence in the McGinnis Creek main-stem remained greater than 8% throughout the sampling period, and was on average more than twice as high as compared to both Fish and Peterson Creek (Fig. 6). Similarly, $SUVA_{254}$ values in the McGinnis Creek main-stem were typically less than half of

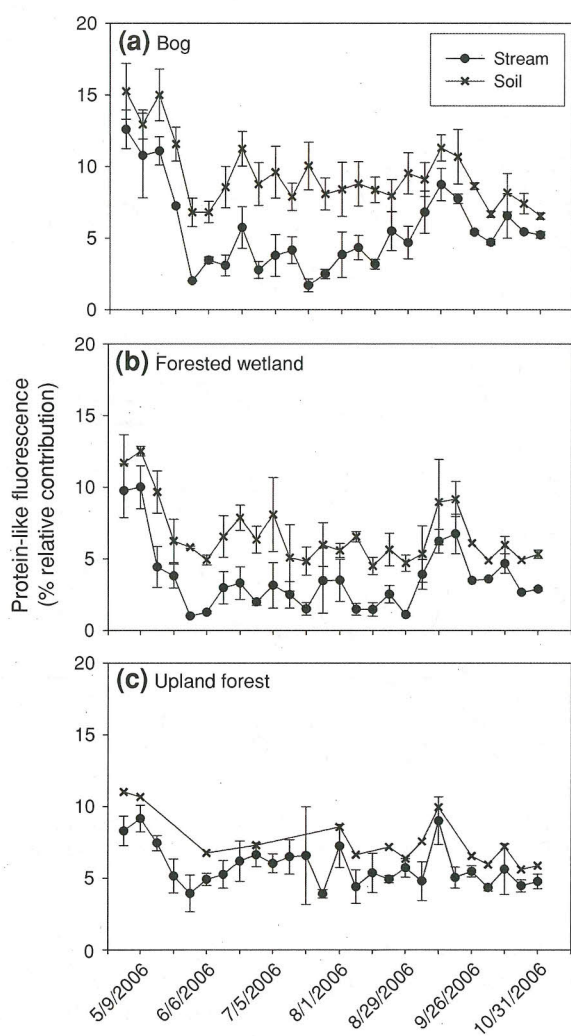


Fig. 4 Time series of protein-like fluorescence (sum of tyrosine and tryptophan-like fluorescent components) for soil water and streamwater in the **a** bog, **b** forested wetland and **c** upland forest during the May through October sampling season. Error bars indicate ± 1 SE and $N = 3$ for each sample date. SE bars are not present for soil water in the upland forest because soil water was frequently unavailable to collect at all three sites

those in Fish and Peterson Creek (Fig. 7). However, when spawning salmon were present in the Peterson Creek main-stem during August, the contribution of protein-like fluorescence increased from approximately 1.5 to $>14\%$ and $SUVA_{254}$ values decreased from 4.4 to 3.5 during the spawning period. Overall, the temporal pattern in protein-like fluorescence and $SUVA_{254}$ in the Peterson Creek main-stem was similar to the pattern observed in the bog and

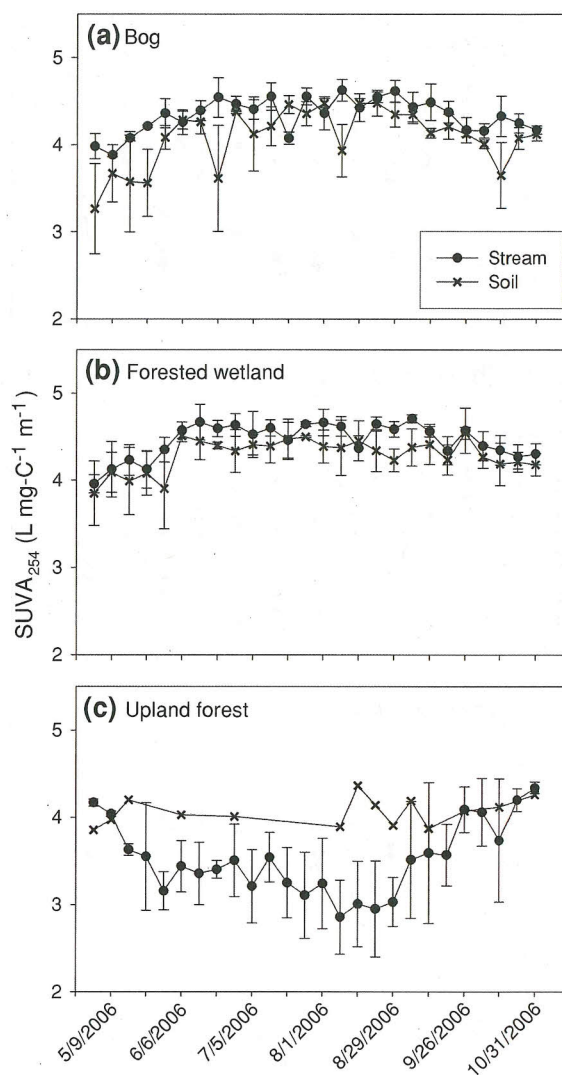


Fig. 5 Time series of $SUVA_{254}$ values for soil and streamwater in the **a** bog, **b** forested wetland and **c** upland forest during the May through October sampling season. Error bars indicate ± 1 SE and $N = 3$ for each sample date. SE bars are not present for soil water in the upland forest because soil water was frequently unavailable to collect at all three sites

forested wetland streams, except during the period when spawning salmon were present.

The contribution of protein-like fluorescence was a strong predictor of percent BDOC in soil and streamwater for all three watersheds throughout the sampling period (Fig. 8a–c). Interestingly, DOM in the Peterson and Fish Creek watersheds generally decreased along the soil–stream continuum, from its source in the soils to the watershed main-stems.

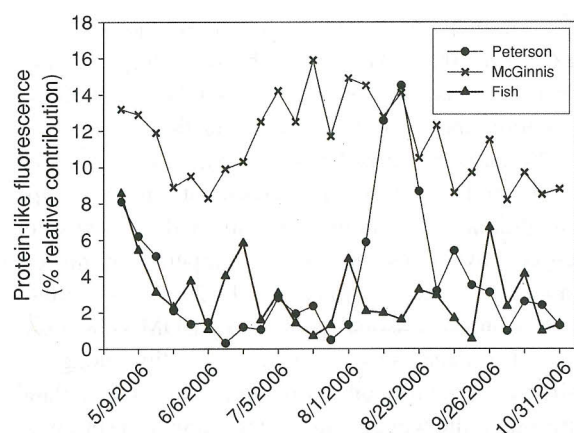


Fig. 6 Time series of protein-like fluorescence (sum of tyrosine and tryptophan-like fluorescent components) for the three watershed main-stems during the May through October sampling season

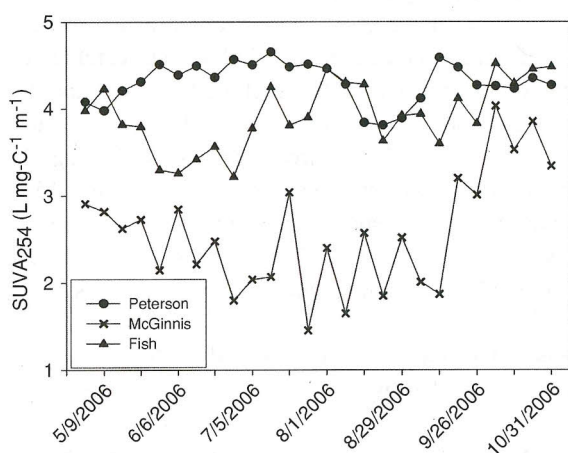


Fig. 7 Time series of SUVA₂₅₄ values for the three watershed main-stems during the May through October sampling season

However, DOM in the McGinnis Creek main-stem was generally more biodegradable than soil water and sub-catchment stream water DOM within the watershed. SUVA₂₅₄ values in wetland soil and streamwater were negatively correlated with percent BDOC ($r^2 = 0.43$, $p < 0.001$, Fig. 9a), although SUVA₂₅₄ was a poor predictor of BDOC in the upland forest sites alone ($r^2 = 0.10$, $p > 0.05$, Fig. 9b). In addition, percent BDOC was positively correlated with DOP ($r^2 = 0.40$, $p < 0.001$) and DON ($r^2 = 0.38$, $p < 0.001$), but poorly correlated with DIN ($r^2 = 0.10$, $p > 0.05$) and SRP ($r^2 = 0.12$, $p > 0.05$) concentrations for all samples taken together.

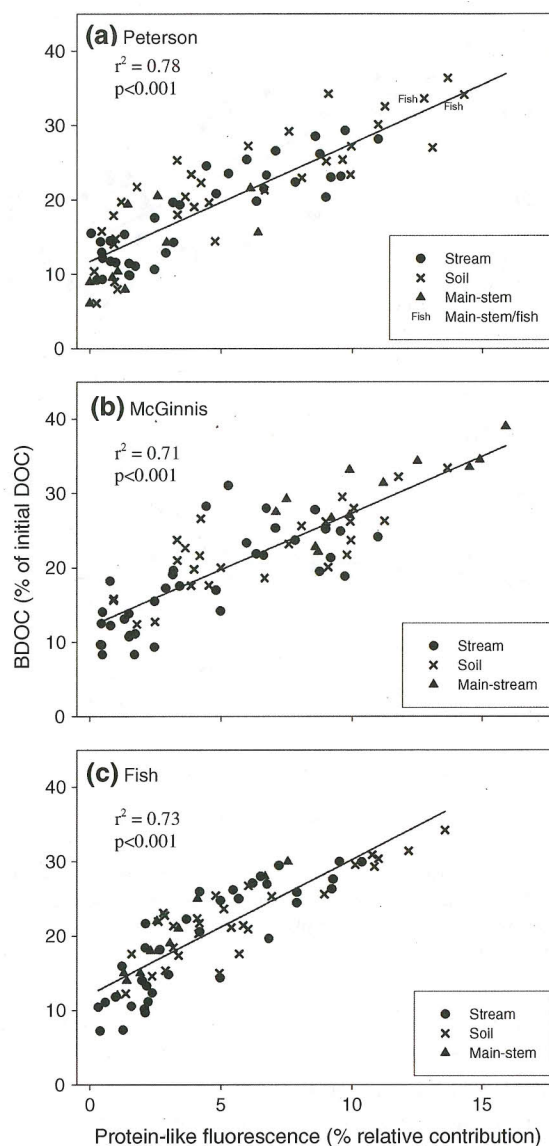


Fig. 8 Regression model describing the relationship between the relative contribution of protein-like fluorescence (sum of tyrosine and tryptophan-like components) and percent BDOC for soil and streamwater in the **a** Peterson Creek, **b** McGinnis Creek, and **c** Fish Creek watersheds during the May through October sampling season. The “fish symbol” in (a) refers to two main-stem samples collected when spawning salmon were present in Peterson Creek

Discussion

Dissolved nutrient concentrations

Our findings underscore the important biogeochemical role of organic N in soil nutrient cycling and

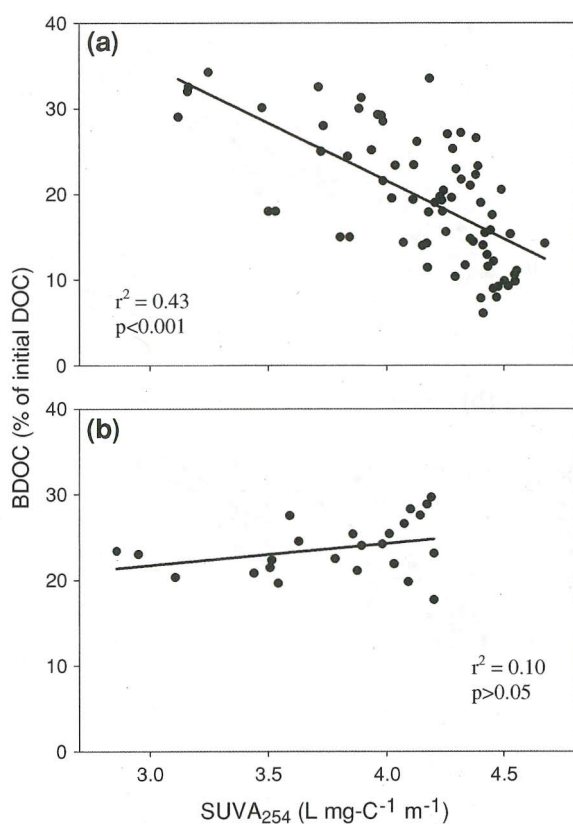


Fig. 9 Regression model describing the relationship between $SUVA_{254}$ values and percent BDOC for the **a** wetland soil and streamwater samples and **b** upland forest soil and streamwater samples only

stream runoff from coastal temperate rainforest (CTR) watersheds, similar to the findings of Hedin et al. (1995). In our wetland study streams, up to 98% of TDN concentrations occurred as organic N, which is as high as seen in other watersheds with significant wetlands (Pellerin et al. 2004). However, in the young and recently deglaciated McGinnis Creek watershed where DIN comprised a substantial portion of stream water N, other factors such as soil C:N ratios (Hood et al. 2003) and the presence of N-fixing plants (Fastie 1995) may control the balance of inorganic vs. organic N concentrations. As with nitrogen, DOP was the dominant form of TDP in our study confirming the importance of organic nutrient forms in CTR watersheds. Conventional wisdom holds that CTR streams are commonly nutrient limited, and the concentrations of inorganic nutrients in our study streams (DIN typically below $10 \mu\text{g N l}^{-1}$ and SRP typically below $4 \mu\text{g P l}^{-1}$; Table 2) are

low enough to limit in-stream production (see Francoeur 2001). Thus, the lability of these organic forms of N and P could strongly influence nutrient limitation and overall stream production.

The large range in DOM concentrations observed in this study indicates that seasonality and soil type can dramatically influence soil and streamwater nutrient dynamics in coastal temperate rainforest watersheds (see Fellman et al. 2008 for further discussion on seasonal patterns in DOM concentration). The decrease in DOC concentration along the soil-stream continuum was greater in the upland forest than the wetland sites suggesting adsorption by the mineral soil horizons (McDowell and Likens 1988) and/or dilution by low DOC water occurred more readily in upland forest than in wetland soils. DOC concentrations in soil water and in outlet streams draining the three soil types were generally greater than those of the main-stem streams, reflecting different source areas within the catchment, spatial differences in the soil carbon pool as the stream flows through different soil types and the removal of DOC by in-stream processes. Average N and P concentrations decreased by more than 55% along the soil-stream continuum in the three soil types, indicating strong biotic control over dissolved N and P loss from the study soils.

Seasonal variation in the chemical quality and biodegradability of DOM

One of the most surprising results of this research was the abundance of labile DOM generated within soil water and transferred to surface waters for all three soil types, particularly in the wetland sites. DOC in the McGinnis Creek main-stem was generally more labile than the Peterson Creek main-stem, but the greater DOC concentrations in Peterson Creek led to high concentrations of BDOC ($0.7\text{--}3.8 \text{ mg l}^{-1}$). Although a large fraction of this wetland-derived DOC was refractory, these BDOC concentrations can exceed DOC concentrations in many temperate streams (Kaplan et al. 2006). Previous research in the east Hudson region of New York found a positive correlation between wetland extent and streamwater concentrations of BDOC (Kaplan et al. 2006). However, this finding was unexpected because wetlands are thought to contribute humic substances to streams that have conventionally been considered recalcitrant

and largely unavailable to bacterial degradation (Geller 1986). Our findings support the idea that wetlands are a source of labile DOM to streams and that these seasonal contributions of BDOC could be an important component of the metabolic stability in downstream aquatic ecosystems.

In the bog and forested wetlands, stream water DOM composition during the spring and fall closely reflected the soil water composition, as demonstrated by the similar contribution of protein-like fluorescence in soil water and in streams. These findings suggest that the tight coupling between wetland DOM source pools and streams was responsible for the delivery of labile DOM to streams. During the spring and fall wet seasons, soil saturation can result in the flow of water through shallow soil layers or at the acrotelm-catotelm interface, as observed in other peatland soils (Worrall et al. 2003). Thus, short DOM soil residence times and low biotic demand can allow labile DOM of recent origin to move into adjacent streams (Schiff et al. 1997; Fraser et al. 2001). Conversely, during the summer growing season, water table drawdown occurs and water flows more slowly through the less permeable catotelm. Increased soil biotic demand and longer DOM residence times result in higher rates of BDOC consumption and the delivery of lower quality DOM to streams. Stream water BDOC increased briefly during the fall wet season as hydrologic flowpaths intersected soil surface horizons and litterfall provided a pulse of BDOC to soil and stream water.

Clear seasonal differences in the chemical quality and lability of DOM from wetlands versus upland forest soils illustrates that these soil types have the potential to alter stream biogeochemical processes differently by influencing temporal patterns in stream productivity. In the bog and forested wetland, soil and streamwater DOM during the spring runoff was the most labile, protein-rich and contained the lowest SUVA_{254} values. This seasonal pattern in BDOC was consistent with other studies of wetlands soils (Wiegner and Seitzinger 2004), and three Alaskan rivers draining into the Arctic Ocean (Holmes et al. 2008). Moreover, the observed spring peak in streamwater protein-like fluorescence was similar to findings on the Williamson River, Oregon where total amino acid concentrations were several times higher in the winter and spring than during the summer months (Lytle and Perdue 1981). Soil microbial cell

lysis during freeze-thaw cycles can increase soil extractable amino acid concentrations (Ivarson and Sowden 1966) and was likely an important source of labile, protein-rich DOM during the spring in CTR watersheds. Freeze-thaw cycles can also cause fine root mortality (Tierney et al. 2001) and increased N mineralization (Schimel and Clein 1996) resulting in a pool of soluble N that is potentially available to flush to streams.

In contrast to the wetland sites, SUVA_{254} values in the upland forest stream were greater during the spring than in the summer. This suggests DOM was more recently leached and aromatic during the spring runoff, which is similar to the seasonal pattern observed on the Yukon River (Striegl et al. 2005). We also observed no strong seasonal pattern in BDOC in soil or stream water in the upland forest, consistent with a study in hardwood forest soils of the Hudson River Valley (Boyer and Groffman 1996). Our findings indicate strong biotic control over DOM composition in wetland soils and streams, although increased abiotic removal, biotic controls and differences in soil hydrologic flowpaths interact to control DOM dynamics in upland forest sites. These contrasting patterns in DOM composition were evident in the predictive relationships for BDOC as SUVA_{254} was positively correlated with BDOC in the wetland sites and poorly correlated with BDOC in the upland forest sites. This suggests that SUVA_{254} may not be the best predictor of DOM lability across different environments, and that other indicators such as protein-like fluorescence (Fig. 8) maybe more useful in predicting BDOC (Fellman et al. 2008).

Changes in DOM lability and chemical quality along the soil-stream continuum

Significant changes in DOM composition were observed along the soil-stream continuum in all three soil types. The observed decrease in SUVA_{254} values as DOM moved from soils to sub-catchment streams for the bog and forested wetland indicates selective removal of the non-aromatic fraction of DOM, consistent with the findings in constructed wetlands in Arizona (Pinney et al. 2000). In contrast to the wetland sites, SUVA_{254} values and the contribution of fulvic-like component 4 increased concomitant with a decrease in the humic-like component 1 along the soil-stream continuum in the upland forest sites.

This corroborates previous research in a northern hardwood forest showing that humic acids typically precipitate out and accumulate in organic horizons, whereas the more mobile fulvic acids move down with percolating water during the spodic soil forming process (Ussiri and Johnson 2003). Our findings indicate that in the upland forest, stream water DOM reflects dilution by low DOM water and the adsorption and/or precipitation of certain fractions of DOM along the soil-stream continuum (Kalbitz et al. 2005).

Patterns in the lability of DOM in the watershed main-stem streams showed that the protein-rich, labile fraction of DOM was selectively removed with passage downstream through the Peterson and Fish Creek watersheds. These findings were similar to those in the Kuparuk River basin in northern Alaska where BDOC progressively decreased with passage through the watershed (Michaelson et al. 1998). Our experimental approach does not allow us to identify specific DOM removal processes. For example, stream DOC additions have shown abiotic sorption can remove substantial DOM (McDowell 1985; McKnight et al. 2002) from the water column. However, the strong correlation between protein-like fluorescence and BDOC and the decrease in the contribution of the humic-like component both strongly suggest biotic removal was modifying DOM composition with passage through the watershed. The exception to this observed pattern in BDOC was when large numbers of anadromous salmon were present in the Peterson Creek main-stem. The peak in BDOC and protein-like fluorescence observed during August strongly reflects salmon contributions of labile DOM to the aquatic DOM load in Peterson Creek (see Hood et al. 2007).

DOM as a source of biologically available N in CTR watersheds?

The hypothesis that DON may be a leak of biologically available N from ecosystems was first introduced by Hedin et al. (1995), who found that DON dominated stream N fluxes in the pristine coastal temperate watersheds of southern Chile. Although this study does not directly address this question, our BDOC incubations and field measurements contribute to the growing body of evidence suggesting that DON may be a leak of biologically available N from ecosystems (see Neff et al. 2003). In our study,

BDOC was correlated with protein-like fluorescence, consistent with lake enrichment studies that have shown microbial uptake of amino acids contributed significantly to microbial C and N incorporation (Tranvik and Jorgensen 1995). Moreover, BDOC incubations with boreal forest soil water showed a selective degradation of protein-like fluorescence while other compounds remained or increased in relative abundance (Wickland et al. 2007). We also found BDOC was poorly correlated with DIN and SRP concentrations, lending support to the idea that microbial communities used organic N and P during our laboratory incubations.

Protein-like fluorescence dropped dramatically in soil and streamwater during the summer growing season in the wetland sites, suggesting rapid uptake of organic N by microbes, vegetation (Chapin et al. 1993) or N mineralization and subsequent uptake of inorganic N (Jaeger et al. 1999). A companion study found net N mineralization rates were low during the summer in these same bog and forested wetland soils (Fellman and D'Amore 2007), also indicating high biotic demand for released N in peatland soils. On the other hand, the cool and wet climate of southeast Alaska may promote low N mineralization rates, and combined with the frequent soil flushing that occurs, the plant and microbial community may be well adapted to short circuit the traditional N cycle by taking up organic forms of N from solution.

We further estimate the biodegradable fraction of DON (BDON) in sub-catchment soil and streamwater using the measured BDOC combined with our TDN concentrations. We assumed: 1) for every 1 mg C l⁻¹ consumed, microbes require 40 ug N l⁻¹ to satisfy growth requirements using a bacterial growth efficiency of 0.4 and a bacterial molar ratio for C:N of 10, and 2) all the available DIN was consumed before the microbial community began utilizing DON. Under these assumptions, we estimated that for soil water 200–320 ug DON-N l⁻¹ or 32–42% of the total pool of DON was consumed during incubations. For sub-catchment streams, 50–130 ug DON-N l⁻¹ or 28–41% of the total DON pool and for main-stem streams 20–65 ug DON-N l⁻¹ or 12–24% of the total pool of DON was consumed during incubations.

These estimates suggest that microbes were using DON as a source of N during our incubations, which has important implications for both terrestrial and downstream aquatic ecosystems in CTR watersheds.

If microbial communities were able to utilize DON to satisfy growth demands, the production of protein-rich, labile DOM and subsequent loss in stream runoff may be an important loss of available N from CTR soils. This loss of amino-acid N may be particularly important in wetland ecosystems because field studies on the arctic sedge *Eriophorum vaginatum* found preferential uptake of amino acids (Chapin et al. 1993), similar to the *Eriophorum* species (e.g. *russeolum*) commonly found in our bog sites. Therefore, we hypothesize that the temporal loss of DON may constrain terrestrial primary production over the long term in CTR watersheds, assuming N inputs were not sufficiently large to offset the loss of DON. On the other hand, downstream aquatic communities may be able to capitalize on these terrestrial inefficiencies and use DON, thereby satisfying growth demands. Overall, our findings imply that terrestrial and aquatic ecosystems were tightly linked by DOM production and consumption processes in CTR watersheds.

Implications for DOM cycling and export from CTR watersheds

Anadromous salmon exert a large influence on their spawning streams by releasing marine-derived nutrients into freshwater aquatic food webs (Chaloner et al. 2002). Our findings indicate that like salmon, wetland soils were important for the biogeochemistry and function of stream ecosystems in the temperate rainforest biome because these carbon rich soils provide inorganic nutrients and abundant labile DOM to downstream aquatic ecosystems. Moreover, unlike salmon, the influence of wetlands on stream water chemistry extends throughout much of the year. We therefore propose that wetland inputs of labile DOM to streams, which can occur both seasonally and episodically during stormflows (Fellman et al. 2009), could be an important component of stream productivity throughout the main runoff season. However, salmon inputs of N and P and DOM augment stream ecosystem productivity during the waning portion of the summer growth season. This nutrient subsidy from spawning salmon occurs at a particularly important time because wetland BDOC inputs to streams were typically quite low during the main spawning periods. Therefore, these complimentary inputs of nutrients and labile DOM from wetlands

and spawning could sustain stream ecosystem productivity through time in CTR watersheds.

Conclusions

The lability and chemical quality of DOM varied temporally and spatially in the three study watersheds. Thus, seasonal changes in terrestrial-aquatic linkages can have a major influence on watershed biogeochemistry with important implications for stream metabolism and the delivery of labile DOM to coastal ecosystems. The progressive downstream decoupling between soil water and stream water BDOC suggests that in small, headwater catchments, soil source pools and DOM in stream water were strongly linked. However, as stream order increases, there was a breakdown or decoupling of the soil-stream continuum. Therefore, the chemical characteristics of streamwater DOM derived from different terrestrial source pools will become more similar to each other with passage through the watershed.

Our findings showed that wetland soils were a source of BDOC to streams and that seasonal changes in BDOC production/removal processes combined with hydrologic transport represent a potential loss of labile DOM from CTR watersheds. Although the land area in southeast Alaska is approximately 29% wetland, individual watersheds are comprised of a mosaic of different wetland and mineral soil types with wetland coverage ranging from <5 to >90% of the total watershed area. Thus, the observed differences in the seasonality and chemical quality of DOM derived from wetlands versus upland forest soils indicates there could be drastic differences in how CTR watersheds cycle and export labile DOM over time.

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