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Watershed Glacier Coverage Influences Dissolved Organic Matter Biogeochemistry in Coastal Watersheds of Southeast Alaska

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Abstract

The Coast Mountains of southeast Alaska are currently experiencing some of the highest rates of glacier volume loss on Earth, with unknown implications for proglacial stream biogeochemistry. We analyzed streamwater for δ^{18}O and dissolved organic matter (DOM) biogeochemistry (concentration, δ^{13}C-dissolved organic carbon (DOC), and fluorescence characterization) during the 2012 glacial runoff season from three coastal watersheds in southeast Alaska that ranged in glacier coverage from 0 to 49% and a glacier outflow stream. Our goal was to assess how DOM biogeochemistry may change as receding glaciers are replaced by forests and glaciers contribute less meltwater to streamflow. Discharge and streamwater δ^{18}O varied seasonally reflecting varying contributions of rainfall and snow/icemelt to streamflow over the runoff season. Mean DOC concentrations were lowest in the glacial outflow and highest in the non-glacial stream reflecting an increasing contribution of vascular plant-derived carbon with decreasing watershed glaciation. Fluorescence and δ^{13}C-DOC signatures indicated that DOM shifted from vascular plant-derived, humic-like material in the non-glacial stream toward more δ^{13}C-DOC enriched, glacier-derived DOM in the glacial outflow. Streamwater δ^{18}O was significantly correlated to DOC concentration, δ^{13}C-DOC, and protein-like fluorescence of streamwater DOM (all $P < 0.05$), demonstrating that changes in the source of streamwater across the glacial watershed continuum have important implications for the amount and quality of stream DOM export. Overall, our findings show that continued glacial recession and subsequent changes in glacial runoff could substantially influence the biogeochemistry of coastal temperature watersheds by altering the timing, magnitude, and chemical signature of DOM delivered to streams.

Key words: glacier change; dissolved organic matter; stable isotopes; fluorescence characterization; fluvial systems; biogeochemistry.

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Introduction

Glaciers are an important source of runoff to fluvial systems in high-elevation and high-latitude ecosystems because these frozen stores of freshwater moderate interannual variability in discharge (Fleming and Clarke 2005), contribute to water resources (Bradley and others 2006), and help maintain high-quality habitat for salmonids and aquatic macroinvertebrates by cooling stream temperature during the summer runoff months (Dorava and Milner 2000; Jacobsen and others 2012; Fellman and others 2014). Mountain and subpolar glaciers have decreased in volume over the last century in many regions worldwide, with some of the largest changes occurring in low-elevation temperate glaciers (Dyurgerov and Meier 2000; Barry 2006). Rates of glacier volume loss are projected to remain steady or increase in most regions of the world (Radic and Hock 2011). This continued loss of ice will both alter watershed landcover, as newly exposed land becomes re-vegetated, and decrease the proportion of streamflow derived from glacial runoff, leading to changes in the biogeochemistry of dissolved organic matter (DOM) delivered to freshwater and near-shore marine ecosystems.

Recent studies of inland waters highlight that DOM cycling along fluvial networks influences carbon cycling on local to global scales (Cole and others 2007; Battin and others 2009), but relatively little is still known about the biogeochemistry of DOM in proglacial streams. This is especially important to ecosystem carbon cycling in regions such as southeast Alaska where glacier runoff accounts for approximately 30% of total land-to-ocean discharge of freshwater (Neal and others 2010). Glacial runoff typically contains DOM that is dominated by aliphatic-rich material and is low in aromatic, lignin-rich material (Hedges and others 2000; Spencer and others 2008; Bhatia and others 2010), even in temperate coastal watersheds where abundant forest commonly occurs on mountain slopes adjacent to glaciers (Hood and others 2009). Potential sources of DOM in glacial environments include soils and vegetation overrun during periods of glacial advance (Hood and others 2009; Bhatia and others 2010, 2013), anthropogenic aerosol deposition (Stubbins and others 2012), and primary production as well as allochthonous carbon input on the glacier surface (Stibal and others 2008; Anesio and others 2009; Stibal and others 2010, 2012). Laboratory bioassays have also shown that glacier-derived DOM is highly bioavailable relative to DOM in non-glacial rivers (Hood and others 2009; Singer and others 2012), underpinning its important role in watershed-scale carbon cycling.

Glaciers connect upland terrestrial ecosystems to freshwater and coastal marine waters through the highly seasonal and spatially variable contribution of glacial runoff to streamflow (Fleming and Clarke 2003, 2005; Stahl and Moore 2006). A common approach for identifying the changing glacial footprint on streamflow is to use a gradient of watersheds that vary in glacier coverage together with stables isotopes of water (δ^{18}O and δ^{2}H) (Mark and McKenzie 2007; Hood and Berner 2009). Snow and glacier ice are often relatively δ^{18}O depleted because of natural fractionation that occurs with increasing elevation and decreasing temperature (Dansgaard 1964). Thus, streamwater δ^{18}O values in proglacial watersheds typically become more depleted with increasing glacier coverage and demonstrate a seasonal depletion as glaciers contribute more meltwater to streamflow relative to other watershed sources, such as groundwater or rainfall (Rietti-Shati and others 2000; Mark and McKenzie 2007; Hood and Berner 2009). However, the seasonal evolution of linkages between glacier hydrology and proglacial stream DOM biogeochemistry, and how they will be impacted by glacier volume loss are still not well understood.

The Coast Mountains of southeast Alaska are currently experiencing some of the highest rates of glacier volume loss on Earth (Larsen and others 2007; Berthier and others 2010). Our goal for this study was to use streamwater δ^{18}O together with measurements of dissolved organic carbon (DOC) concentration and DOM quality (δ^{13}C-DOC and fluorescence characterization) to determine how DOM biogeochemistry may change as receding glaciers are replaced by forested ecosystems and glaciers contribute less runoff to streamflow. To accomplish this, we collected streamwater weekly to fortnightly during the glacial runoff season of 2012 from three watersheds in coastal southeast Alaska that ranged in glacier coverage from 0 to 49%. We also sampled the outflow stream from Herbert Glacier to evaluate the DOM biogeochemistry of glacial runoff. This scheme allowed us to assess how changes in watershed glaciation influence the cycling and exchange of organic matter between terrestrial, freshwater, and coastal marine ecosystems.

Methods

Site Description

Streamwater was collected from three watersheds along the Juneau road system in coastal southeast Alaska (Figure 1). Juneau is located on the western margin of the 3,800 km^2 Juneau Icefield, which blankets the Coast Mountains of northern Southeast Alaska. Juneau has a cool, maritime climate with persistent cloud cover and a mean average temperature of 4.7°C at sea level. Glacier recession has sculpted the region leaving a mosaic of landscape features including glaciers, high alpine, water-logged peatlands, and forested mineral accumulations over bedrock and glacial till (D'Amore and others 2012).

The three study watersheds (Herbert, Cowee, and Peterson) range in area from 24 to 152 km^2 and contain much of the variation in landcover typical of coastal watersheds draining west to the Gulf of Alaska. The Herbert River watershed, which contains a major outflow glacier from the Juneau Icefield (Herbert Glacier), is heavily glaciated (49% watershed glacier coverage). The glacier outflow sample site was located at the terminus of the Herbert Glacier approximately 10 km upstream from the Herbert River sample site. Cowee Creek contains two hanging glacier complexes and is lightly glaciated (13% watershed glacial coverage). The upper reaches of both glacial watersheds are characterized by recently deglaciated terrain with extensive high alpine tundra, exposed bedrock, poorly developed soils, and little vascular plant vegetation. Although average watershed elevation is 860 m in Herbert River and 638 m in Cowee Creek, the glacial rivers are low gradient (<5%) downstream near the point of streamwater collection and contain few braided side channels. The landscape in the mid to lower reaches of the glacial watersheds is older consisting of mixed coniferous forest of *Picea sitchensis* and *Tsuga heterophylla* with small areas of wetland. Peterson Creek is a low-gradient, wetland-dominated watershed with a small lake near the headwaters. The watershed has no glacier ice and a mean watershed elevation of 309 m. The landscape is mainly mixed coniferous forest of *P. sitchensis* and *T. heterophylla* with large

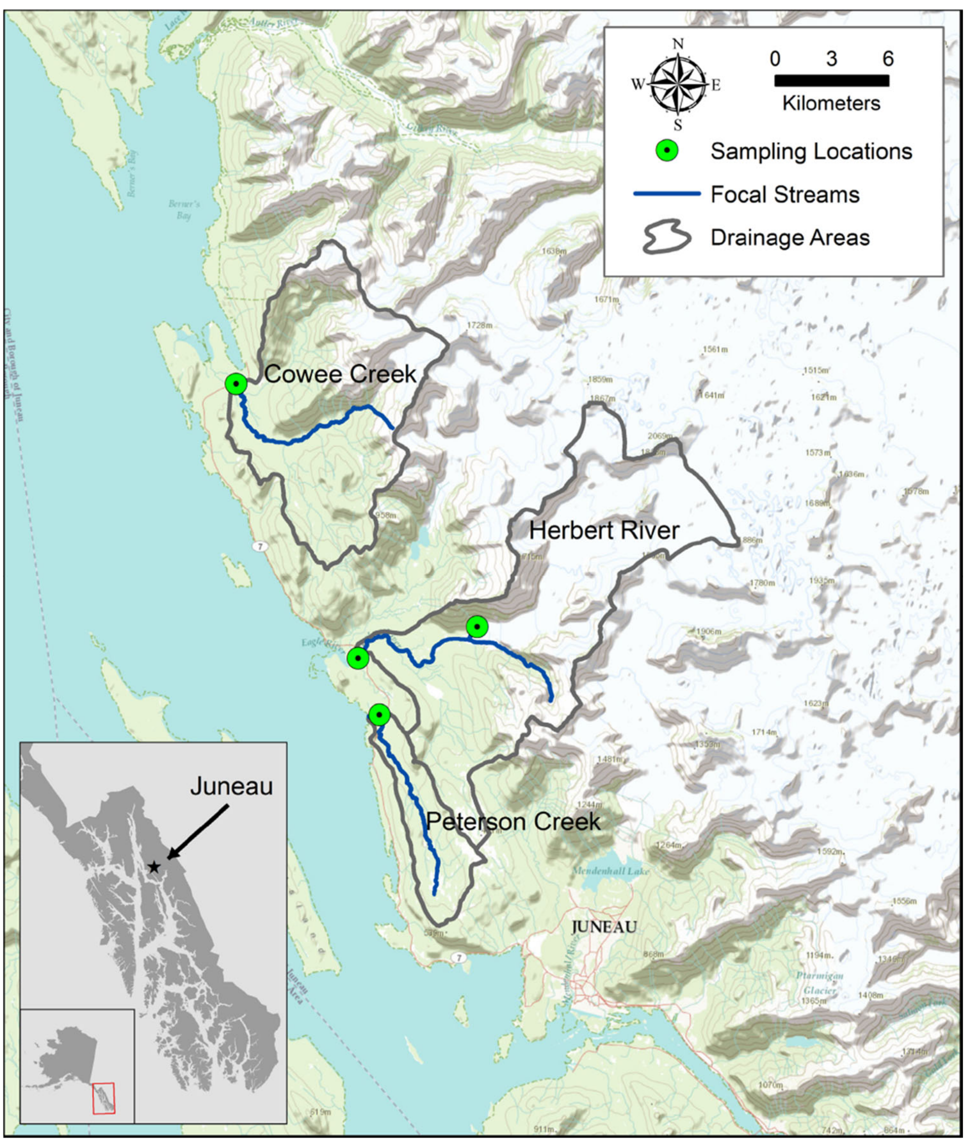

Figure 1. Map of the three study watersheds and sampling sites near Juneau, Alaska (Color figure online).

areas of forested and unforested peatland. The stream channel is characterized by a sequence of riffles and pools where wetted-widths generally range from 5 to 10 m in the lower reaches of the watershed.

All three watersheds have anadromous Pacific salmon runs (*Oncorhynchus* spp.) lasting from late June through September, which vary in spawner density and species. In particular, Herbert River has low densities of spawning salmon throughout the summer. However, high spawning salmon densities occur in Cowee Creek in mid-August through September and Peterson Creek during July and August where carcass densities can be as high as 3.5 kg m^{-2} (Hood and others 2007). Consequently, salmon have been shown to deliver large quantities of nutrients (Mitchell and Lamberti 2005; Chaloner and others 2004) and DOM to the study streams that has an unique fluorescence fingerprint enriched in protein-like relative to humic-like fluorescence (Hood and others 2007; Fellman and others 2008).

Sample Collection

Surface water was collected weekly from the three stream sites (Cowee, Herbert, and Peterson) and fortnightly from the Herbert glacier subglacial outflow from early May, 2012 until the last week of October, 2012. All water samples were filtered in the field sequentially through AquaPrep 600 filters (Pall Life Sciences, 0.45 µm) followed by Whatman Polycap 36TC filters (0.20 µm). Prior to sample collection, the filters were pre-cleaned with hydrochloric acid, flushed with Milli-Q water, and primed with sample water. Rainfall (for $\delta^{18}O$) for ten different events greater than 10 mm was also collected during the measurement period near the lower Herbert River site. Rainfall was collected using a glass bottle and plastic funnel immediately following an event to minimize evaporative water loss.

Mean air temperature at the Juneau airport (<50 km from all sites) during the 6-month study period was 9.4°C (range −5.5 to 19.3°C), which is below the long-term May–October average of 10.8°C. Rainfall for the study period (1013 mm) was above the long-term average of 870 mm at the Juneau airport. However, rainfall in October, 2012 was less than half (88.9 mm) of the long-term average of 219 mm. Discharge in Peterson Creek was measured at 15-min intervals for the study period using a stilling well equipped with a pressure transducer (Solinst Levelogger Gold model 3001) and the stage–discharge relationship was used to calculate streamflow. Discharge in Cowee Creek is measured by the Alaska Department of Fish and Game. For Herbert River, we used historical discharge data from the previous U.S. Geologic Survey (USGS) stream gage site at Herbert River (#15054200) to develop a regression model with data from the long-term USGS gage site at Mendenhall River (#15052500). The regression model was used to calculate discharge in Herbert River based on Mendenhall River discharge data from the study period. Four spot measurements of discharge were made at Herbert River to confirm the derived relationship between Herbert and Mendenhall River.

Dissolved Organic Carbon Analysis and Flux Calculation

Samples for DOC (determined by high-temperature non-purgeable organic carbon analysis) were collected in pre-combusted amber glass vials, stored at 4°C, and measured on a Shimadzu TOC-V CSH analyzer within 48 h of collection (Stubbins and Dittmar 2012). A high sensitivity catalyst was used to enable the detection of low DOC concentrations. Daily fluxes of DOC were calculated with daily average discharge and weekly DOC measurements ($N = 26$) using LoadRunner software to automate the U.S. Geologic Survey LoadEstimator program (Runkel and others 2004). The LoadEstimator program finds a best fit calibration regression, which is then applied to the daily discharge data to obtain daily DOC loads. The Akaike Information Criteria were used to select the model that best fits the data.

Water Isotopes and Characterization of DOM

A 25 ml water sample was collected for $\delta^{18}O$ analysis at all sites to assist in identification of the different water sources contributing to streamflow. Water isotope samples were stored in glass bottles with zero headspace at room temperature until analysis on a Picarro L2120-*i* analyzer within 1 month of collection. Values for $\delta^{18}O$ are reported in per mil (‰) after normalization to Vienna standard mean ocean water (VSMOW; Paul and others 2007). The fluorescence characteristics of DOM were measured on a Fluoromax-4 (Jobin Yvon Horiba) scanning fluorometer following the methods of Hood and others (2007). Water samples were analyzed at room temperature and absorbance at 254 nm was measured on a Genesys 5 spectrophotometer with a 5 cm pathlength. If necessary, samples were diluted according to Green and Blough (1994) to minimize inner filter effects.

Excitation–emission matrices (EEMs) were collected by measuring fluorescence intensity across excitation wavelengths from 240 to 450 nm (5 nm increments) and emission wavelengths from 300 to 600 nm (2 nm increments). All EEMs were corrected for instrument bias and Raman normalized using the area under the water Raman peak at excitation 350 nm (Stedmon and others 2003).

Parallel factor analysis (PARAFAC) was used to analyze the EEMs using the PLS_toolbox version 3.7 in MATLAB (Eigenvector Research 2006) following the procedures of Stedmon and others (2003). The data array used in the model consisted of 160 EEMs with 151 emission and 43 excitation wavelengths. Excess Raman and Rayleigh scatter were removed from the EEMs before modeling by adding a series of zeros to the region under both scatter peaks. PARAFAC components were reported as either a F_{max} in Raman units (RU), or as a percent relative contribution determined by quantifying the contribution of each component and dividing that by the total fluorescence of all the modeled PARAFAC components within a sample.

Our PARAFAC model identified a total of five fluorescence components (4 humic-like and 1 protein-like) and was validated using split-half analysis (Stedmon and others 2003). The spectral characteristics of the five fluorescence components were similar to those of other studies in freshwater and glacial environments (Barker and others 2006, 2009; Jaffe and others 2008; Dubnick and others 2010). Humic-like components 1–4 (C1–C4) all have emission maxima at wavelengths greater than 420 nm, and are considered to be derived predominantly from terrestrial plant and soil organic matter (Stedmon and others 2003; Stedmon and Markager 2005; Cory and McKnight 2005). The fluorescence characteristics of protein-like C5 (Ex = 270 nm, Em = 346 nm) were similar to a reference standard of tryptophan. This component commonly dominates the fluorescence spectra in glacial environments (Barker and others 2006; Dubnick and others 2010).

Results

Streamflow and Water $\delta^{18}O$ Analysis

Mean daily specific discharge and $\delta^{18}O$ values in the three study watersheds were used to evaluate seasonal changes in streamwater sources, particularly glacier runoff. Mean daily specific discharge in non-glacial Peterson Creek ranged from less than 0.1 to 1.2 mm h^{-1} and generally decreased from early May to its summer minimum in late July before rebounding during the late summer/early fall rainy season (Figure 2A). Although specific discharge in glacier-fed Cowee Creek and Herbert River showed numerous rainfall spikes similar to Peterson Creek, the seasonal hydrograph strongly reflected snow and ice-melt contributions to streamflow during the summer glacial runoff period. For instance, mean daily specific discharge in the two glacial streams was lowest in early May followed by an overall increase until early August when both streams reached their maximum mean weekly flow (>0.8 mm h^{-1}) during the study period. Overall, the 6-month study period accounted for greater than 90% of the annual discharge in both Cowee Creek and Herbert River.

Streamwater $\delta^{18}O$ values reflected a gradient of increasing watershed glaciation with seasonal mean values becoming increasingly enriched with increasing watershed glacier coverage: -13.7 ± 0.1‰ for Peterson Creek, -15.1 ± 0.1‰ for Cowee Creek, -15.4 ± 0.1‰ for Herbert River, and -16.4 ± 0.1‰ for the Herbert Glacier outflow (Figure 2B). Streamwater $\delta^{18}O$ in Peterson Creek

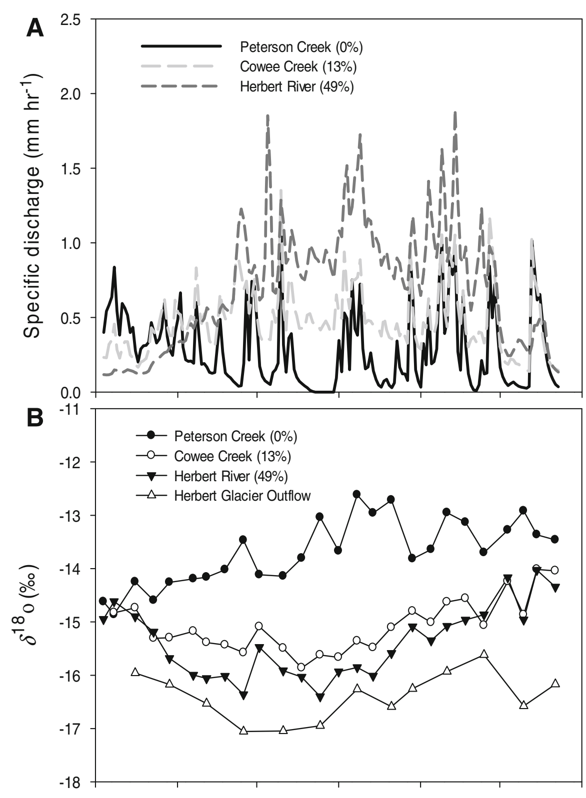

Figure 2. **A** Mean daily specific discharge (mm h^{-1}) and **B** $\delta^{18}O$ values (‰) for the three study watersheds (% glacial coverage) during the 1 May through 31 October, 2012 study period.

increased from early May to its summer maximum in August as a result of the combined influence of groundwater inputs to streamflow and evapo-fractionation during periods of low flow. The two glacial streams and glacial outflow showed a similar seasonal pattern to that of discharge where streamwater $\delta^{18}O$ values decreased from early May to their meltwater-influenced (snow and glacier ice) minima in late July before increasing again in late summer. Despite the wide range in $\delta^{18}O$ observed during the main glacial runoff period, values in the three stream sites were comparable during early May and were becoming more similar to each other in October during which time streamwater $\delta^{18}O$ values were closest to the seasonal mean $\delta^{18}O$ signature of rainfall ($-11.4 \pm 0.7‰$, $N = 10$).

Streamwater DOC Concentration and Flux

Concentrations of DOC in Peterson Creek were always above 4.0 mg C l^{-1} but were consistently elevated (>8.0 mg C l^{-1}) during August and September (Figure 3A). In contrast, DOC in the two glacial streams was generally below 1.0 mg C l^{-1} except during May and September/October when concentrations exceeded 1.5 mg C l^{-1}. Concentrations of DOC in the Herbert Glacier outflow and Herbert River site were similar during the main glacial runoff season of mid-June through mid-August, but concentrations in the glacier outflow remained below 0.4 mg C l^{-1} during May and October even when concentrations in Herbert River were above 2.5 mg C l^{-1}. Across all sites, we report a significant non-linear relationship between streamwater $\delta^{18}O$ values and concentrations of DOC ($R^2 = 0.84$, $P < 0.01$) reflecting the strong coherence between DOC concentration and changing sources of streamwater across the watershed glaciation gradient (Figure 4A).

Daily specific DOC fluxes in Peterson Creek ranged from less than 1 to 315 kg km^{-2} day^{-1} and tracked closely with precipitation reflecting the large frontal storms that are typical of mid-summer and fall (Figure 3B). Daily specific DOC fluxes in Herbert River were overall the lowest in magnitude and variability of the three sites even though daily specific discharge was generally the greatest. This pattern is consistent with the very low DOC concentrations observed in the heavily glaciated site during the summer runoff season. Specific fluxes of DOC from Cowee Creek also tracked closely with precipitation and were in general intermediate in magnitude between the other two stream sites reflecting a gradient in watershed glacial coverage. Overall, mean monthly specific DOC fluxes were greatest in September for all sites: 114 kg km^{-2} day^{-1} for Peterson Creek, 33 kg km^{-2} day^{-1} for Cowee Creek, and 25 kg km^{-2} day^{-1} for Herbert River.

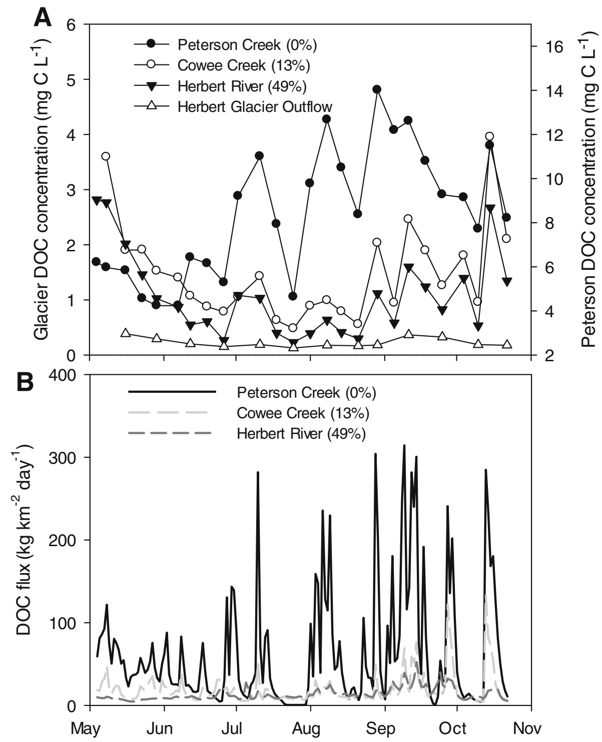

Figure 3. Time series of **A** streamwater DOC (mg C L^{-1}) for the three glacial sites and the non-glacial Peterson Creek (right *Y*-axis) and **B** DOC flux (kg km^{-2} day^{-1}) for the three stream sites during the 1 May through 31 October, 2012 study period.

Spectroscopic and Isotopic Characteristics of DOM

Humic-like components (sum of C1–C4) were the largest contributor to total DOM fluorescence in all sites, particularly in the non-glacial Peterson Creek, but to a much lesser extent in the glacial outflow (Figure 5A). Humic-like fluorescence in the glacial sites showed a seasonal patter similar to that of DOC where F_{max} values were highest during early May and October and lowest during the main glacial runoff period of July and August. The F_{max} values for protein-like fluorescence (C5) showed no strong seasonal pattern for any of the sites and mean values generally increased with decreasing glacial coverage (Figure 5B). However, Cowee Creek and especially Peterson Creek showed several spikes in protein-like fluorescence (both percent and F_{max} values) during late July and August (Figure 5B, C) that can largely be attributed to the

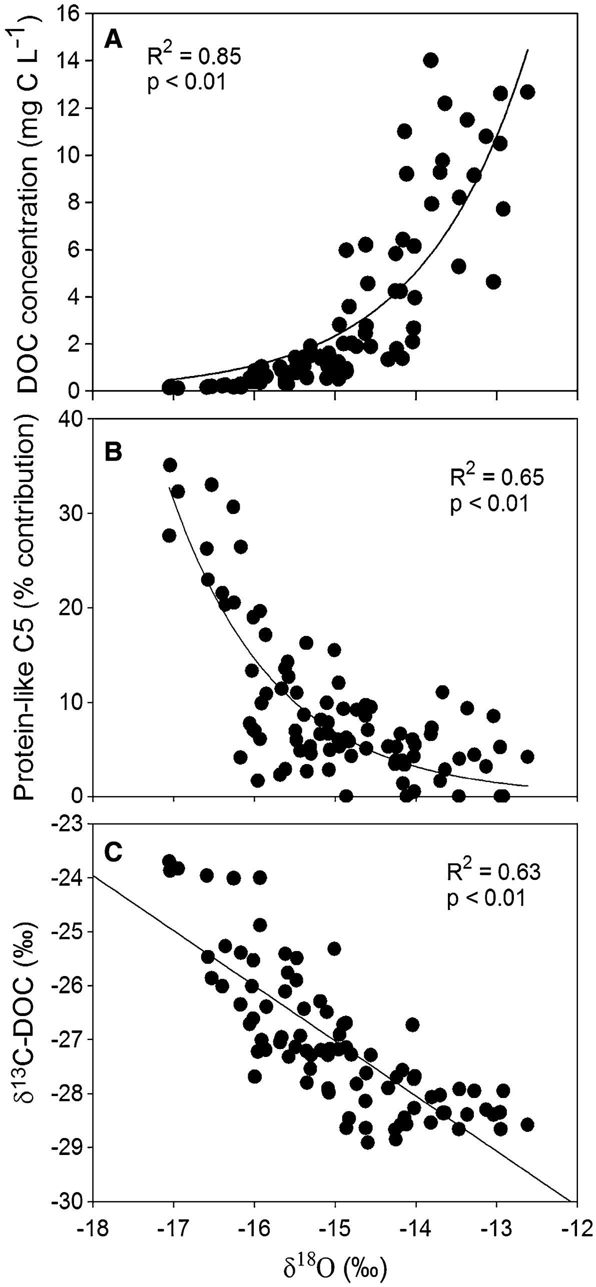

Figure 4. Regression models describing the relationships between streamwater δ^{18}O (‰) and concentrations of **A** DOC (mg C l^{-1}), **B** the percent contribution of protein-like fluorescence (C5), and **C** δ^{13}C-DOC (‰). Concentrations of DOC were log transformed for statistical analysis to satisfy assumptions of normality and equal variance.

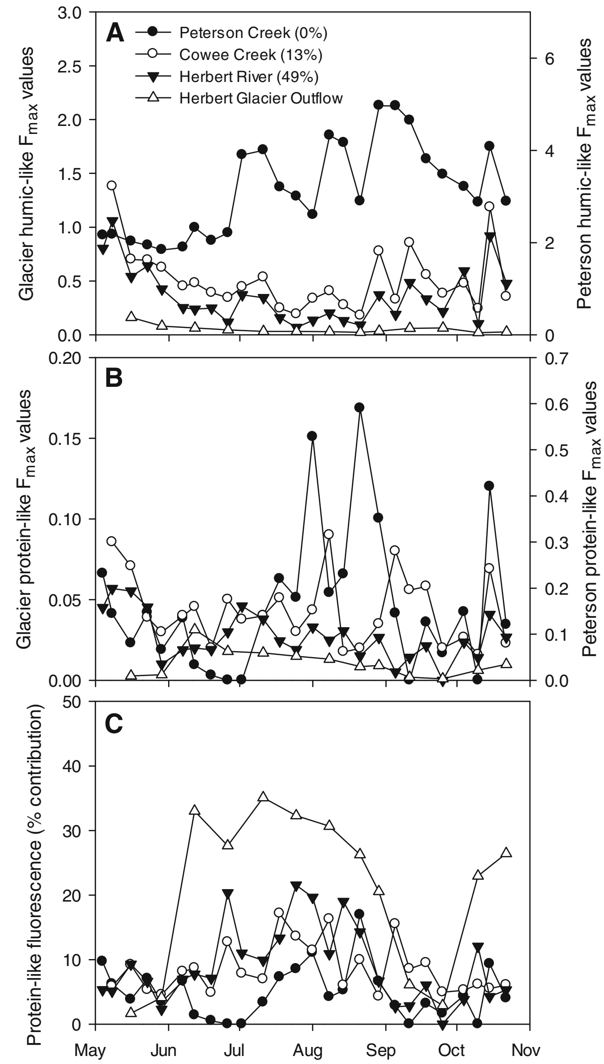

Figure 5. Time series of **A** humic-like F_{max} values (sum of C1–C4) for the three glacial sites and the non-glacial Peterson Creek (right *Y*-axis), **B** protein-like F_{max} values (C5) for the three glacial sites and the non-glacial Peterson Creek (right *Y*-axis), and **C** the percent contribution of protein-like fluorescence (C5) for the four study sites during the 1 May through 31 October, 2012 study period.

release of organic nitrogen from spawning salmon (Hood and others 2007; Fellman and others 2008). In Peterson Creek, these spikes in protein-like fluorescence occurred during periods of low streamflow, which intensifies the influence that spawning salmon have on DOM biogeochemistry (Hood and others 2007).

The percent contribution of protein-like fluorescence showed a contrasting pattern to that of its F_{max} values where mean values were 4.9 ± 0.8% for Peterson Creek, 8.6 ± 0.8% for Cowee Creek, 9.0 ± 1.2% for Herbert River, and 20.8 ± 3.5% for the Herbert Glacier outflow (Figure 5C). Consequently, DOC concentrations were positively related to F_{max} values for protein-like fluorescence (R^2 = 0.47, $P < 0.01$, data not shown) but negatively related to percent protein-like fluorescence for all sites together ($R^2 = 0.53$, $P < 0.01$, data not shown). Therefore, as glaciers contribute less meltwater to streamflow relative to other sources, DOC concentrations increase along with protein-like F_{max} values but percent protein-like fluorescence decreases.

Mean δ^{13}C-DOC values showed a substantial enrichment with increasing watershed glacier coverage: −28.4 ± 0.1‰ for Peterson Creek, −27.1 ± 0.1‰ for Cowee Creek, −26.7 ± 0.2‰ for Herbert River, and −24.9 ± 0.3‰ for the glacier outflow (Figure 6). The δ^{13}C-DOC values for Peterson Creek were always less than 27.9‰, except on one sample date in August when spawning salmon were abundant and likely contributed DOM to the stream that was enriched in δ^{13}C-DOC (Figure 6) and protein-like fluorescence (Figure 5B) relative to other watershed sources. In the glacial sites, δ^{13}C-DOC showed a strong seasonal pattern similar to that of percent protein-like fluorescence, with the most depleted values during early May and October and more enriched values during the main glacial runoff period of July and August. Cowee Creek also showed a substantial enrichment in δ^{13}C-DOC and spikes in protein-like fluorescence in mid-August and early September which was likely due to salmon contributions of ^{13}C-enriched DOM. With the exception of May and early June, δ^{13}C-DOC values in Herbert River were typically substantially depleted (>1.7‰) relative to the glacier outflow. Streamwater δ^{18}O values were also significantly correlated with the percent contribution of protein-like fluorescence ($R^2 = 0.65$, $P < 0.01$, Figure 4B) and δ^{13}C-DOC values ($R^2 = 0.63$, $P < 0.01$, Figure 4C), reflecting the influence of shifting streamwater sources on the isotopic and fluorescence signature of streamwater DOM.

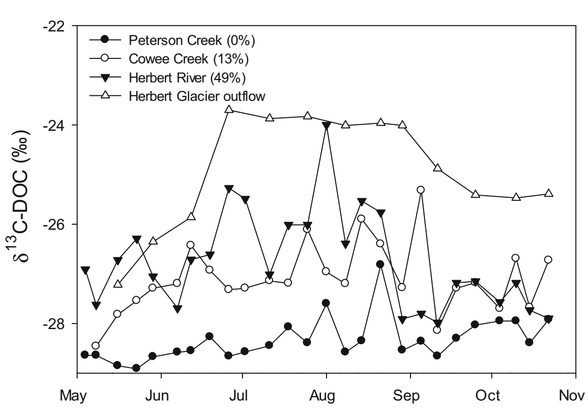

Figure 6. Time series of streamwater δ^{13}C-DOC (‰) for the four study sites during the 1 May through 31 October, 2012 study period.

Discussion

Influence of Glacial Runoff on DOM Biogeochemistry

The seasonal patterns in discharge in the three watersheds and the increasingly depleted δ^{18}O signature associated with increasing glacier coverage highlight how watershed hydrology differs between non-glacial and glacial watersheds in terms of both the timing and source of discharge (Fountain and Tangborn 1985; Fleming 2005). Hydrologic models predict that although glacial retreat may result in an initial increase in annual runoff and streamflow, extended glacier retreat will cause a shift in flow regime similar to that of non-glacial watersheds, with discharge becoming more responsive to storms and more vulnerable to extreme low flow events during warm and dry periods (Fleming and Clarke 2005; Stahl and Moore 2006; Stahl and others 2008). In our study, δ^{18}O values in the three glaciated sites remained depleted well into the summer months of July and August in contrast to non-glacial Peterson Creek where values increased during this same period. The most pronounced isotopic enrichment observed in Peterson Creek coincided with periods of severe low flow likely reflecting increased inputs of δ^{18}O-enriched groundwater. These findings underscore the importance of glacial meltwater inputs for maintaining streamflow during the summer runoff period in temperate forested watersheds. This is particularly ecologically relevant in regions such as southeast Alaska and the Pacific Northwest of the USA where glacial meltwater moderates stream temperature in coastal watersheds that support abundant salmonid runs during the summer months (Dorava and Milner 2000; Fellman and others 2014).

Our finding that δ^{18}O values were significantly related to DOM biogeochemistry (Figure 4) provides clear and quantitative evidence of the link between catchment water sources (glacial versus non-glacial) and the dynamics of the streamwater DOM pool. In particular, the increasingly depleted streamwater δ^{18}O values resulting from inputs of glacier and snow-melt (Mark and McKenzie 2007; Hood and Berner 2009) were associated with lower concentrations and specific fluxes of stream DOC. Moreover, DOC concentration showed a non-linear increase as streamwater δ^{18}O values became more enriched suggesting that even small changes in catchment water sources can substantially influence the streamwater DOM pool. Glacial outflow DOC also showed low variation relative to non-glacial Peterson Creek (coefficient of variation of 0.1 for the glacial outflow and 0.4 for Peterson Creek) during the mid-summer (June through August) glacial runoff period. This suggests that there is less variability in the concentration of DOM when glacier runoff contributes substantially to streamflow. These findings collectively show that measurements of stable isotopes of water may be useful for estimating the concentration and chemical quality of DOM in regions where streamwater DOM is derived from landscape source pools (for example, glaciers, wetlands) that have unique isotopic signatures. In this context, shifts in δ^{18}O in space and time could provide information about changes in the magnitude and chemical character of riverine DOM.

Streamwater DOC concentrations in Peterson Creek were consistently elevated (>4.0 mg C l^{-1}) and humic-like components dominated DOM fluorescence, except when spawning salmon were present in the stream during July and August. These results clearly reflect the high wetland coverage in the watershed (Hood and others 2007; Fellman and others 2009), and support other research showing that wetland-derived DOM has a high aromatic C content (Gondar and others 2005; Agren and others 2008) and is dominated by humic-like fluorescence (Stedmon and others 2003; Baker and Spencer 2004; Hood and others 2007). Similarly, our finding that F_{max} values for protein-like fluorescence generally increased with decreasing glacier coverage was not surprising because total fluorescence increases with increasing DOC concentration and terrestrially derived DOM generally contains some protein-like fluorescence (Cory and others 2007; Fellman and others 2009), especially DOM leached from fresh plant material (Wickland and others 2007). Furthermore, our findings show that even in wetland-dominated watersheds where the streamwater pool of DOM is derived mainly from terrestrial plant material, salmon episodically influence the biogeochemistry of their spawning streams by releasing DOM enriched in protein-like fluorescence and δ^{13}C.

The glacial streams in contrast typically had low concentrations (<1.5 mg C l^{-1}) and specific yields of DOC (<50 kg km^{-2} day^{-1}), had a greater percent contribution of protein-like fluorescence, and more enriched δ^{13}C-DOC values compared to non-glacial Peterson Creek. These patterns result from the poorly developed soils, low soil organic matter content, and the lack of vascular plants that can contribute abundant DOM to proglacial streams (Tockner and others 2002; LaFreniere and Sharp 2004). Glacier snow and ice-melt contain very little organic matter (DOC concentration ~0.1–0.2 mg C l^{-1}) and protein-like fluorescence typically dominates the little DOM fluorescence that exists (Barker and others 2009; Dubnick and others 2010; Stubbins and others 2012). This confirms previous studies showing that glacier-derived DOM is ''microbial'' in character (low molecular weight and aromatic C content) and is enriched in protein-like fluorescence relative to ice-free areas (Lafreniere and Sharp 2004; Barker and others 2009; Dubnick and others 2010). These results together show that as glaciers recede and are replaced by forested and wetland ecosystems, streams accumulate DOM (low in percent protein-like fluorescence and enriched in humic-like material) that is derived mainly from landscape sources of terrestrial plant material. Thus, DOM quality in proglacial streams becomes more similar to non-glacial streams as watershed glacial coverage decreases.

There were also differences in the temporal dynamics of DOM biogeochemistry between glacial and non-glacial sites. For instance, DOC concentrations in Peterson Creek were consistently elevated during the late summer and early fall wet season as a result of the flushing of aromatic, high molecular weight DOM from the abundant wetlands in the watershed (Hood and others 2007; Fellman and others 2009). On the other hand, the glacial streams showed a decrease in DOC concentration and δ^{13}C-DOC values became more enriched (-23 to -25‰) during the summer months (mid-June through mid-August) when glacial runoff is at its maximum. However, during the spring and fall months when glacial meltwater contributes less to streamflow relative to other landscape sources (for example, groundwater), DOM chemical signatures shifted toward more terrestrial-like, as indicated by an increase in F_{max} values for humic-like fluorescence and a decrease in percent protein-like fluorescence and δ^{13}C-DOC values. Although DOM chemical signatures can be highly variable, due to the interaction of dynamic water source contributions (Brown and others 2006; Blaen and others 2012), hydroclimatological conditions (Brown and others 2006; Blaen and others 2012), and the presence of spawning salmon (Hood and others 2007), our findings show that DOM chemical signatures follow generally consistent seasonal patterns based largely on catchment landcover (for example, presence of wetlands, glaciers).

Large rainfall events, which are abundant in this region and likely to increase in occurrence with climate warming, appear to influence streamwater DOM chemical signatures across the glacial watershed continuum by flushing aromatic, vascular plant-derived DOM to streams (Fellman and others 2009). For example, DOC concentrations (Figure 2A) and humic-like fluorescence (Figure 5A) in the glacial watersheds (Cowee and Herbert) increased more than threefold from the previous sample date during a large storm in mid-October. These results indicate that as contributing DOM source areas change during large storms, abundant terrestrially derived DOM can be flushed to glacial streams because a greater fraction of water flows through forest soils that are rich in organic carbon rather than glacier ice and till. These findings support the notion that mass-balance driven shifts in ice volume which alter glacier runoff will alter the chemical signature of DOM at the watershed scale (Hood and Scott 2008).

Ecosystem Implications for Continued Watershed Deglaciation

Our findings highlight how glaciers connect upland terrestrial landscapes to freshwater and coastal marine waters, linking DOM biogeochemistry in fundamentally different environments. In particular, we found streamwater DOM reflects gradients in concentration and chemical quality with a shift from more protein-like material (low molecular weight, non-aromatic) in the subglacial outflow toward more aromatic, vascular-plant derived in the non-glacial Peterson Creek. These results are consistent with the model of landscape evolution for watersheds undergoing deglaciation in Glacier Bay, southeast Alaska where the increase in streamwater DOM over time is due mainly to the flushing of vascular plant-derived DOM from the developing terrestrial landscape (Engstrom and others 2000; Milner and others 2007). These findings further suggest that even though the study watersheds varied dramatically in their dominant soil type, underlying geology, and extent of wetlands and glaciers, streamwater varied systematically in its biogeochemical properties and seasonal dynamics. Therefore, we suggest that continued loss of glaciers in the region will have a steady and predictable impact on the chemical signature of stream DOM by altering seasonal streamflow patterns and increasing the amount of vascular plant-derived DOM delivered to aquatic ecosystems. This, in turn, could influence aquatic food web structure by altering the main sources and biological reactivity of organic carbon inputs to recipient freshwater and coastal marine ecosystems.

It is widely recognized that terrestrial subsidies of nutrients and DOM are vital to the productivity of freshwater and coastal marine ecosystems (Findlay and others 1992; Berggren and others 2010; Cole and others 2011). Laboratory bioassays have shown that glacier-derived DOM is highly bioavailable relative to non-glacial DOM (Hood and others 2009; Singer and others 2012). This has caused increased attention (for example, Stibal and others 2012) with respect to the role of glaciers in downstream carbon cycling because of the size of the flux, the high bioavailability of glacial organic carbon, and the future projections for glacier volume loss (Radic and Hock 2011). Although the ongoing loss of glacial ice from coastal watersheds in southeast Alaska could result in a decrease in bioavailable DOM delivered to coastal marine ecosystems (Hood and Scott 2008; Hood and others 2009), our findings and others show that specific DOC yields from forests and/or wetlands are far greater relative to glaciated watersheds (Hood and Scott 2008). Hence, continued glacial recession could result in an increased flux of bioavailable DOM, although this flux will have a lower percentage of bioavailable carbon. However, it is still unclear how watershed deglaciation will affect overall bioavailable DOM fluxes to proglacial streams and the metabolic stability of freshwater and coastal marine ecosystems.

Overall, our findings show that over the long term if glaciers continue to recede and contribute less meltwater to streamflow, there will be a shift in the magnitude of glacier-derived DOM delivered to freshwater and coastal marine ecosystems. We propose that coastal glacial watersheds that contribute freshwater and DOM to the Gulf of Alaska are key contributors to regional carbon cycling. However, this role may change over the coming decades as glaciers recede and are replaced by forested and alpine ecosystems. Quantifying annual and seasonal bioavailable DOM yields from forests and glaciers could help elucidate how watershed land cover influences DOM delivery and ultimately organic carbon utilization in the Gulf of Alaska.

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