Riverine organic matter and nutrients in southeast Alaska affected by glacial coverage

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The delivery of fresh water, carbon, nitrogen and phosphorous from high-latitude regional watersheds is important to the ecology and nutrient balance of coastal marine ecosystems in the Northern[1] and Southern[2] hemispheres. Bioavailable dissolved organic matter from rivers can support microbes in near-shore environments, and may also stimulate primary production[3,4]. Recent studies suggest that impacts of climate change, such as thawing permafrost, may affect nutrient yields in large northern rivers[5]. Here we analyse riverine dissolved organic matter and nutrient loads in three adjacent coastal watersheds along the Gulf of Alaska. We find that different levels of glacial coverage can alter the timing and magnitude of fresh water, dissolved organic matter and nutrient yields. Our results suggest that a lower extent of glacial coverage within a watershed can lead to higher amounts of dissolved organic matter, but decreased phosphorous yields. Moreover, an abundance of early successional plant species following deglaciation can increase riverine nitrogen levels. We conclude that changes in riverine yields of dissolved organic matter and nutrients due to reductions in glacier extent in coastal watersheds may affect the productivity and function of near-shore coastal ecosystems.

Mountain glaciers are currently thinning and retreating throughout the globe as a result of climate warming[6]. However, glacial retreat is particularly acute along the Gulf of Alaska (GOA), where there is abundant ice at elevations close to tide water. In the last decade of the twentieth century, glacier ice was lost from this region at a rate of approximately $90\,km^3\,yr^{-1}$, which constituted a greater contribution to sea level rise ($\sim 0.25\,mm\,yr^{-1}$) than runoff from the Greenland ice sheet[7]. The melting of glacier ice is increasing stream flow in coastal glacial watersheds in southeastern Alaska[8], and has important implications for circulation in both coastal fjords[9] and the greater GOA[10]. However, there are very few reports of nutrient yields from glacial watersheds[11]; thus, it is difficult to assess the consequences of glacial recession for riverine biogeochemical fluxes into glacially influenced, near-shore marine ecosystems along the GOA.

We used measured discharge and frequent year-round sampling to quantify riverine yields of C, N and P for three adjacent watersheds in southeastern Alaska with glacial coverages of 0%, 25% and 55%. The differences in glacial coverage across the watersheds enable us to evaluate how changing glacial coverage alters yields of organic and inorganic nutrients from coastal temperate watersheds. Our three study watersheds, Montana Creek, Lemon Creek and the Mendenhall River, are located near Juneau, Alaska and are representative of the thousands of moderately sized coastal watersheds (30–500 km^2) along the GOA. Each watershed contains high-elevation reaches with alpine tundra, exposed bedrock and relatively thin (<1 m) soils, whereas the lower elevations are largely forested with wetlands present in low-gradient terrain and along slope breaks. The three watersheds vary in both watershed area and glacial coverage (Fig. 1), but share similar bedrock lithology.

We found that daily specific yields of dissolved organic matter (DOM) and nutrients during the dominant runoff season between May–November are strongly influenced by glacial melt water. In 2006, daily yields of dissolved organic carbon (DOC) were typically lowest in the glacier-dominated Mendenhall River watershed (Fig. 2), which is consistent with the very low DOC concentrations found in glacial rivers during the summer runoff season[12,13]. Yields of DOC from non-glacial Montana Creek tracked more closely with precipitation, whereas daily DOC yields in Lemon Creek were intermediate in both magnitude and variability. All three watersheds showed multiple transient increases in yields of DOC in response to large frontal storms from the GOA, particularly during the autumn rainy season. However, differences in land cover and hydrology mediated very different DOC responses across the sequence of watersheds. The sharp, pulsed increases in daily DOC yields in Montana Creek are consistent with rapid flushing of allochthonous DOC from terrestrial sources into the stream channel[14], including enhanced DOC mobilization from abundant peatlands and forested wetlands[15]. In contrast, water flow through temperate glaciers is channelized and occurs through englacial pathways[16] that provide little opportunity to mobilize DOM through contact with carbon-rich organic soils. As a result, the peaks for daily fluxes of DOC in response to storm events were broader and less pronounced in the glacial watersheds.

On monthly and annual timescales, specific runoff and yields of C, N and P vary widely in their responses to land-cover differences across the three watersheds. Specific runoff is substantially higher in the glaciated watersheds, particularly during May–October, when the bulk of glacier melting occurs (Fig. 3a). In Mendenhall River, well over half the summer stream flow is derived from glacial melt water, and the high water yields in both Mendenhall River and Lemon Creek are augmented by the ongoing rapid loss of ice

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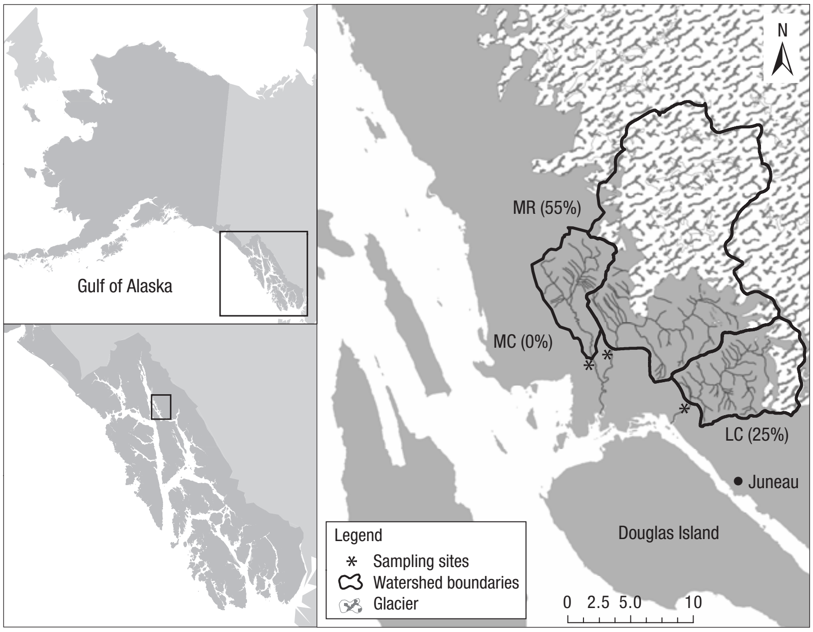

Figure 1 Map of glacier coverage within the study watersheds in southeastern Alaska. Three watersheds, Montana Creek (MC), Lemon Creek (LC) and Mendenhall River (MR), were sampled within 3 km of their estuaries. Percentage of watershed glacier coverage is shown in parentheses. All three watersheds are continuously gauged by the US Geological Survey. Long-term discharge records and approximately weekly sampling during 2006–2007 were used to calculate daily, seasonal and long-term mean annual DOM and nutrient yields.

from their watershed glaciers, which are thinning at rates of up to 4–6 m yr^{-1} at lower elevations[17].

Trends for monthly yields of DOC are opposite those for water, with increasing yields as glacial coverage decreases (Fig. 3b). The difference is particularly pronounced in autumn, when stream flow and concentrations of DOC in forested watersheds in southeastern Alaska are at a maximum. On an annual basis, the DOC yields increase significantly with decreasing glacial coverage among the study watersheds (Fig. 3b). In contrast to DOC, monthly yields of dissolved organic nitrogen (DON) differ little across the three watersheds (Fig. 3c). In the glacial watersheds, DON yields closely track water yields, suggesting that glacial runoff is an important contributor to DON yields. Annual yields of DON show no trend with watershed glacial coverage; however, standard errors for watershed DON yields increase with glacial coverage. Because the magnitudes of the standard errors from our load estimates are dependent on the strength of the concentration–discharge relationship for DON, this finding indicates that the correlation between DON concentrations and discharge becomes weaker as watershed glacial coverage increases. The ratio of annual DON yields to annual DOC yields also increases with watershed glacial coverage (Fig. 3b,c). The relatively high yields of DON as compared with DOC in the two glacial watersheds are consistent with an internal source of DON linked to subglacial drainage[11]. The origin of this DON is probably protein-rich DOM derived from subglacial microbial populations[12,13]. Moreover, the poor relationship between DON concentrations and discharge in the glacial watersheds suggests that release of microbial DON in glacial streams may be similar to other subglacially derived constituents such as suspended sediment, yields of which are flow-path dependent and commonly out of phase with runoff[18].

Unlike organic N, yields of dissolved inorganic nitrogen (DIN) show significant differences among the three watersheds. The non-glacial Montana Creek watershed exhibits low yields of DIN throughout the year except for a period in autumn when high water yields coupled with low biotic demand lead to higher DIN fluxes (Fig. 3d). Overall, this is consistent with DON being the dominant vector of N loss in unpolluted temperate forest watersheds[19]. The highest watershed yields of DIN occur in the moderately glaciated Lemon Creek watershed, which has seen approximately 3.5 km of glacial recession since the end of the Little Ice Age[20]. The recently deglaciated portions of Lemon Creek contain abundant transitional vegetation, and studies of ecosystem succession in nearby Glacier Bay indicate that vegetation on newly exposed soils is dominated by *Dryas drummondii* and *Alnus sinuate* (Sitka alder) for up to a century following deglaciation[21]. These N-fixing species enhance nitrogen mineralization and soil N pools in terrestrial ecosystems[22]. Moreover, N inputs from alder have been shown to produce very high rates of nitrate N export in stream water[23], which is consistent with the high yields of DIN from the Lemon Creek watershed. Yields of DIN in the Mendenhall River generally follow water yields. The DIN yields we report for Mendenhall River are consistent with estimates in other glaciated watersheds[11,24] and probably reflect the low rates of inorganic N deposition in southeastern Alaska ($\leqslant$0.6 kg ha^{-1} yr^{-1}; NADP Network).

Yields of soluble reactive phosphorus (SRP) peak during summer when glacial runoff is at a maximum (Fig. 3e). Glaciated watersheds typically have high yields of total P, much of which is associated with poorly weathered, calcite/apatite-rich mineral phases[25]. In our watersheds, concentrations of SRP increase with glacial coverage, suggesting that a portion of the total P derived from glacial weathering occurs in dissolved forms. Although annual yields of SRP are not significantly different across the three watersheds, the two glacial watersheds have significantly higher yields of SRP compared with Montana Creek during the glacial runoff season (May–October; $p < 0.05$). The higher yields of SRP in the glacial streams during summer (July–September) are probably a function of both higher glacial weathering and lower in-stream

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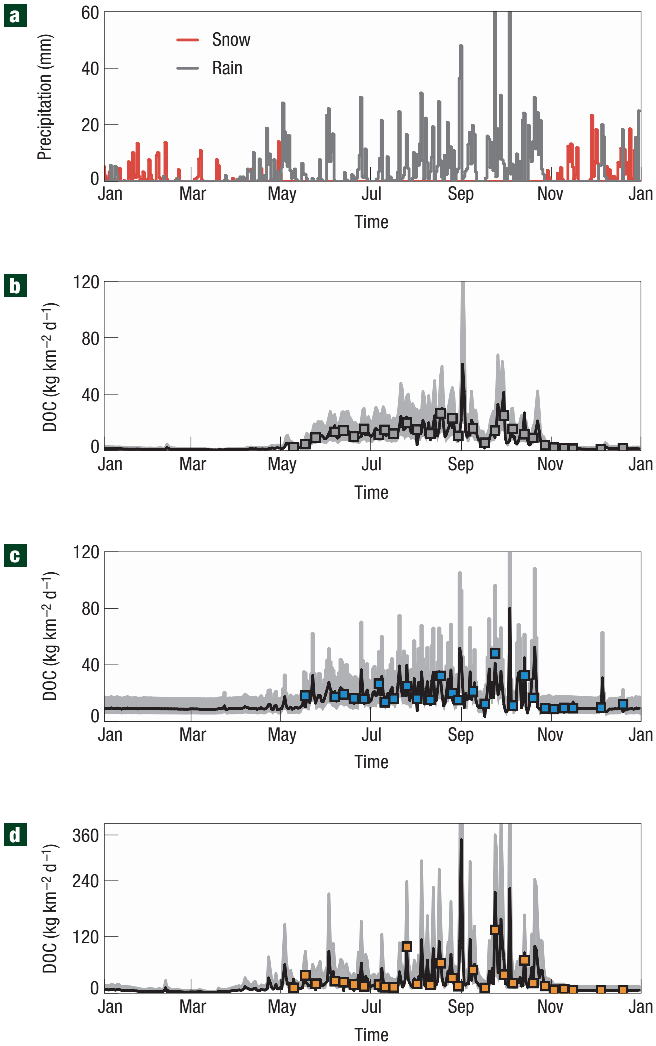

Figure 2 Daily precipitation and DOC yields for 2006. a, Precipitation recorded from NOAA's Juneau airport station shows typical precipitation maxima in September and October. **b–d**, Estimated daily DOC yields (solid dark lines) with 90% confidence intervals (in grey) for Mendenhall River (**b**), Lemon Creek (**c**) and Montana Creek (**d**) illustrate differences in the variability and magnitude of yields across the three watersheds. Note that DOC yields for Montana Creek (no glacier coverage) were plotted on a larger scale compared with the glaciated watersheds. Measured yields for sample dates (shown as squares) captured both seasonal variation and hydrologic variability.

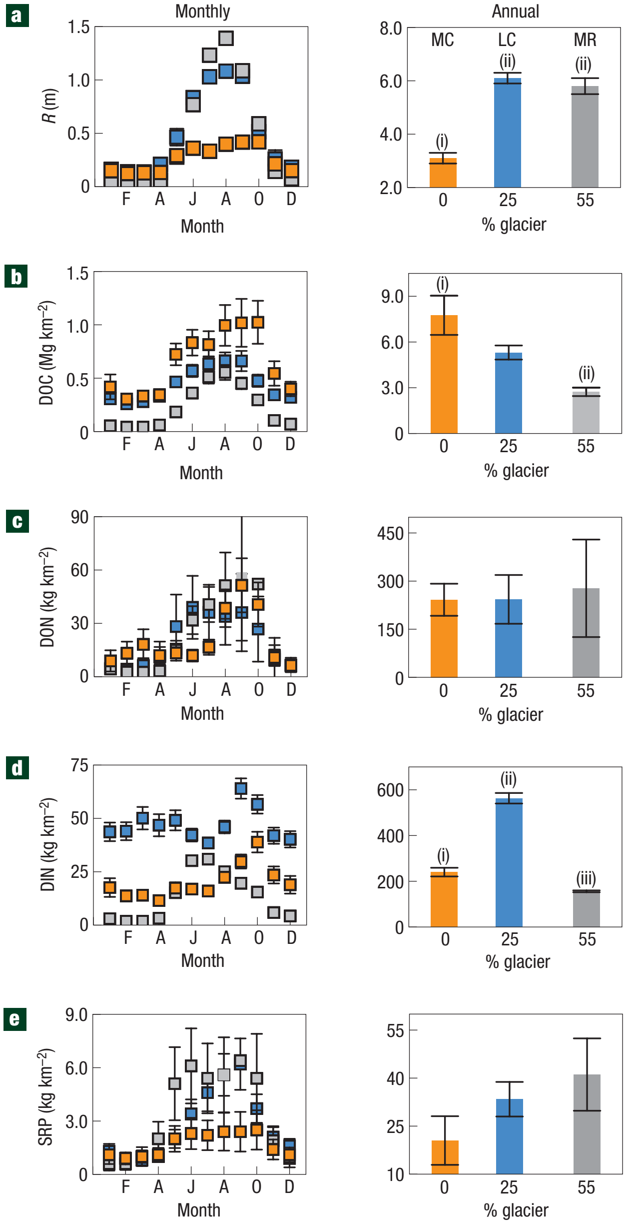

Figure 3 Long-term mean monthly and annual yields for the three study watersheds. a, Mean annual runoff, *R*, highlights the influence of glacier melting between June and September for Lemon Creek (blue symbols) and Mendenhall River (grey symbols) in contrast with Montana Creek (orange symbols). **b–e**, Yields of DOC (**b**), DON (**c**), DIN (**d**) and SRP (**e**) were calculated using weekly sampling and the long-term discharge records for the three watersheds. The error bars on the yields represent one standard error. Annual yields that are significantly different at $p < 0.005$, based on Bonferroni-adjusted post hoc tests, are marked by different roman numerals. Note different units (megagrams) for DOC.

uptake of P through primary productivity, which is strongly limited by scouring and light availability in highly turbid glacial streams[26].

A particularly novel finding of our study is that trends in annual fluxes of DOC and DON are decoupled across our sequence of watersheds, indicating that glacial recession may affect the elemental composition of riverine DOM. The ratio of DOC/DON is a standard measure of the bioavailability of DOM because this ratio shows a strong inverse correlation with DOM lability[27]. Moreover, the $\delta^{18}O$ value of stream water can be used as a relative indicator of the contribution of glacial runoff to stream flow because melt water from snow and glacier ice is depleted in $\delta^{18}O$ compared with other sources of stream flow such as precipitation and ground water[28]. The limited data from our sites demonstrate a very strong correlation between the C/N ratio of DOM and the $\delta^{18}O$ of stream water during the primary runoff season (Fig. 4). This finding suggests that as glaciers recede and contribute less to stream flow, there will be a decrease in riverine export of the more labile (low C/N) pools of DOM that are a potentially important resource for heterotrophs in near-shore marine ecosystems[3,4].

Taken together, our results indicate that decreasing watershed glacial coverage leads to lower riverine yields of fresh water, inorganic P and labile DOM. Thus, it is possible that the ongoing

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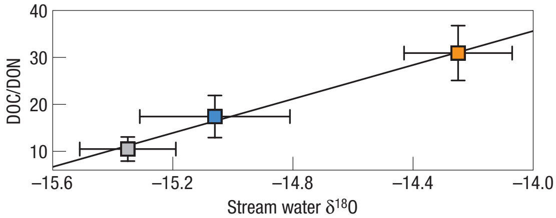

Figure 4 Relationship between δ^{18}O of stream water and DOC/DON ratio of DOM. Error bars represent one standard error. Both isotopic values and DOC/DON ratios are averages for the summer/autumn runoff period (June–September) when the majority of river discharge occurs in all three watersheds owing to climatic forcings (energy for glacial melt and frontal storm events).

loss of glacier ice in watersheds along the GOA[7,17] may substantially alter riverine material yields. Glaciers are also important hydrologic buffers in these watersheds because during dry periods glacial melt water can compensate for decreasing yields of water from the non-glaciated portions of a basin[29]. We suggest that on a seasonal and interannual basis glacial runoff may stabilize the delivery of N and P to marine ecosystems by preventing the pronounced decreases in dry-season riverine nutrient yields seen in non-glacial catchments.

Our findings also indicate that the successional trajectory of terrestrial ecosystems following deglaciation is an important control on watershed yields of organic C and inorganic N. In our watersheds, replacement of glacier ice by coastal temperate rainforest seems to markedly increase riverine fluxes of DOC. In coastal forests in southeastern Alaska, wetland soils are the principal source of DOC in stream water during base flow and storm events[15]. Thus, the extent to which terrestrial succession culminates in peatland and forested wetland landscapes as opposed to upland forest and high-elevation tundra and bedrock will determine the magnitude of the increase in watershed yields of DOC following deglaciation. Our study also suggests that the colonization of transitional plant species during deglaciation may substantially increase yields of DIN from coastal watersheds. The magnitude of this increase will largely be determined by the spatial extent and temporal duration of colonization by N-fixing plant species, which are influenced by multiple factors including the rate of glacial recession and the proximity of seed sources for colonizer species[30].

Overall, our study raises the possibility that glacial recession and associated land-cover change in coastal watersheds may strongly alter land-to-ocean fluxes of organic and inorganic nutrients. The potential for decreased fluxes of labile DOM derived from glacial watersheds is of particular interest and would probably have the most pronounced impacts on near-shore marine ecosystems that have limited mixing with the open ocean, such as those found along fjord/archipelago coastlines in southeastern Alaska, southern Chile and New Zealand. These findings highlight the need for broader comparative studies and long-term sampling programmes to enhance our understanding of biogeochemical cycling of C, N and P across terrestrial/marine ecotones in both hemispheres that are being altered by glacial recession.

METHODS

Streams were sampled weekly from May to November 2006 and approximately biweekly during lower flows from December 2006 to April 2007. At each site, composite samples were obtained from three grab samples collected from a well-mixed region of the stream, and filtered in the field using precombusted 47 mm GF/F filters (0.7 μm). Water for isotope analyses was stored at 4 °C in 25 ml glass bottles, and samples for DOM and nutrient analyses were frozen and stored in 150 ml high-density polyethylene bottles. The filtered stream water was measured for DOC, total dissolved nitrogen (TDN), nitrate nitrogen (NO_3–N), ammonium nitrogen (NH_4–N) and SRP using high-temperature combustion (DOC and TDN), ion chromatography (NO_3–N) and colourimetry (NH_4–N and SRP). DON was calculated as TDN minus inorganic N (NO_3–N + NH_4–N). The δ^8O of stream water was analysed at the Institute of Arctic and Alpine Research Stable Isotope Laboratory on a dual-inlet mass spectrometer, and all δ^8O values are expressed relative to Vienna-standard mean ocean water.

Discharge values for Montana Creek and Mendenhall River were acquired from the US Geological Survey (site numbers 15052800, 15052500; 20 years daily Q). Discharge for Lemon Creek was acquired by using two years of discharge data at the sampling site, and the record was expanded using daily discharge from a long-term US Geological Survey station (15052000, 9 years daily Q) 4 km upstream. For each river, trend-adjusted annual and monthly nutrient loads were calculated using Fluxmaster (http://pubs.usgs.gov/tm/2006/tm6b3/PDF/tm6b3_titlepages.pdf). Here, a base year of 2006 was used with load estimates derived from the relationship between the logarithm of nutrient concentration and the logarithm of daily discharge, with sine and cosine time functions to account for seasonal fluctuations. Standard errors for each estimate were calculated within the model, including the effects of finite sampling and unaccounted factors affecting the concentration–discharge model. One-way analysis of variance tests with Bonferroni multiple comparisons (SPSS statistical software) were used to evaluate differences among watershed yields of DOM and nutrients.

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Author contributions

E.H. designed the study, participated in and guided the field sampling campaigns, and analysed water samples. E.H. and D.S carried out data analysis and D.S. did the watershed yield modelling. E.H. wrote the manuscript with substantial contributions from D.S.

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