Vol 462|24/31 December 2009|doi:10.1038/nature08580

LETTERS

Glaciers as a source of ancient and labile organic matter to the marine environment

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Riverine organic matter supports of the order of one-fifth of estuarine metabolism[1]. Coastal ecosystems are therefore sensitive to alteration of both the quantity and lability of terrigenous dissolved organic matter (DOM) delivered by rivers. The lability of DOM is thought to vary with age, with younger, relatively unaltered organic matter being more easily metabolized by aquatic heterotrophs than older, heavily modified material[2–4]. This view is developed exclusively from work in watersheds where terrestrial plant and soil sources dominate streamwater DOM. Here we characterize streamwater DOM from 11 coastal watersheds on the Gulf of Alaska that vary widely in glacier coverage (0–64 per cent). In contrast to non-glacial rivers, we find that the bioavailability of DOM to marine microorganisms is significantly correlated with increasing ^{14}C age. Moreover, the most heavily glaciated watersheds are the source of the oldest (~4 kyr ^{14}C age) and most labile (66 per cent bioavailable) DOM. These glacial watersheds have extreme runoff rates, in part because they are subject to some of the highest rates of glacier volume loss on Earth[5]. We estimate the cumulative flux of dissolved organic carbon derived from glaciers contributing runoff to the Gulf of Alaska at 0.13 ± 0.01 Tg yr^{-1} (1 Tg = 10^{12} g), of which ~0.10 Tg is highly labile. This indicates that glacial runoff is a quantitatively important source of labile reduced carbon to marine ecosystems. Moreover, because glaciers and ice sheets represent the second largest reservoir of water in the global hydrologic system, our findings indicate that climatically driven changes in glacier volume could alter the age, quantity and reactivity of DOM entering coastal oceans.

Biogeochemical cycling in coastal margins near riverine outflows is dominated by the influx of terrestrial organic matter and nutrients. The effect of anthropogenic increases in nutrient export on sensitive systems is well-documented in regions such as the Gulf of Mexico zone of hypoxia[6]. It is much less clear how climate-induced shifts in the export of terrigenous DOM will affect coastal environments, although the reactivity of this carbon will be key as the extent of its incorporation into marine food webs depends largely on its chemical character[7]. Riverine DOM is typically dominated by allochthonous material derived from plant detritus, which may be substantially aged and degraded before entering the marine environment, thereby reducing its availability to marine heterotrophs[3]. Glacial ecosystems are devoid of higher plants but contain abundant microbial communities adapted to extreme temperature, light and nutrient regimes[8]. Thus, we hypothesize that glacial watersheds export chemically distinct DOM compared to DOM derived from litter and soil organic matter in forested watersheds.

The Gulf of Alaska (GOA) drainage basin contains more than 10% of the mountain glaciers on Earth[5], and annual runoff from this region represents the second largest discharge of freshwater to the Pacific Ocean[9,10]. Along the GOA, watersheds dominated by glaciers have extremely high water fluxes (commonly >6 m yr^{-1}), such that yields of DOM from these watersheds are substantial[11] even with the low concentrations of DOM typical of glacial ecosystems[12,13]. Future changes in glacial runoff are markedly larger than those projected for other components of the water cycle, and the continued recession of GOA glaciers with climate warming is expected to shift the timing and magnitude of riverine DOM delivery to downstream coastal ecosystems[11].

In this study we characterized the source, bioavailability and magnitude of the DOM flux from glacial watersheds that drain into the GOA. We sampled streamwater DOM from 11 coastal watersheds in three geographic areas along the GOA during peak glacial runoff (Fig. 1). All three study areas are located in coastal temperate rainforest biomes characterized by maritime climates, with mean annual sea level temperatures ranging from 2.5 to 4.5 °C. The 11 watersheds are largely free of human disturbance, and land cover is dominated by coniferous forest in the lower elevations of all of the watersheds. Glacier coverage varied markedly (0–64%) within the watersheds owing to differences in elevation and distance from the ocean. Here we use glacier cover as a relative estimate of the proportion of streamwater derived from glacial runoff in each watershed. All riverine water samples were collected above tidal influence within 6 km of tidewater. In addition to measuring bulk dissolved organic carbon (DOC), we used fluorescence spectroscopy, the vascular plant biomarker lignin, and carbon isotopic analyses ($\delta^{13}C$ and $\Delta^{14}C$) to evaluate the chemical character, source and age of riverine DOM exported from the 11 watersheds.

Streamwater DOC concentrations ranged from 0.6 to 2.2 mg C l^{-1} and were negatively correlated with watershed glacier coverage (Table 1; $r^2 = 0.63$, $P = 0.003$). This is consistent with higher inputs of soluble carbon from forest soils in the watersheds with lower glacier coverage[13]. Fluorescence spectroscopy and $\delta^{13}C$-DOC measurements both indicated that increased inputs of glacial meltwater were associated with an increase in the proportion of DOM derived from microbial sources. DOM fluorescence associated with proteinaceous material was positively correlated with watershed glacier coverage (Table 1; $r^2 = 0.82$, $P = 0.001$), indicating that DOM in heavily glaciated watersheds has a high protein content and relatively low concentrations of aromatic organic compounds that typically dominate streamwater DOM[14]. The $\delta^{13}C$ values for streamwater DOC ranged from −25.6‰ to −22.0‰ and similarly demonstrated significant enrichment with increasing watershed glacier coverage (Table 1; $r^2 = 0.53$, $P = 0.01$). The $\delta^{13}C$-DOC values in the heavily (>40%) glacial watersheds were all enriched compared to the range for C_3 plant-derived carbon (about −25 to −30‰)[3,15], which is

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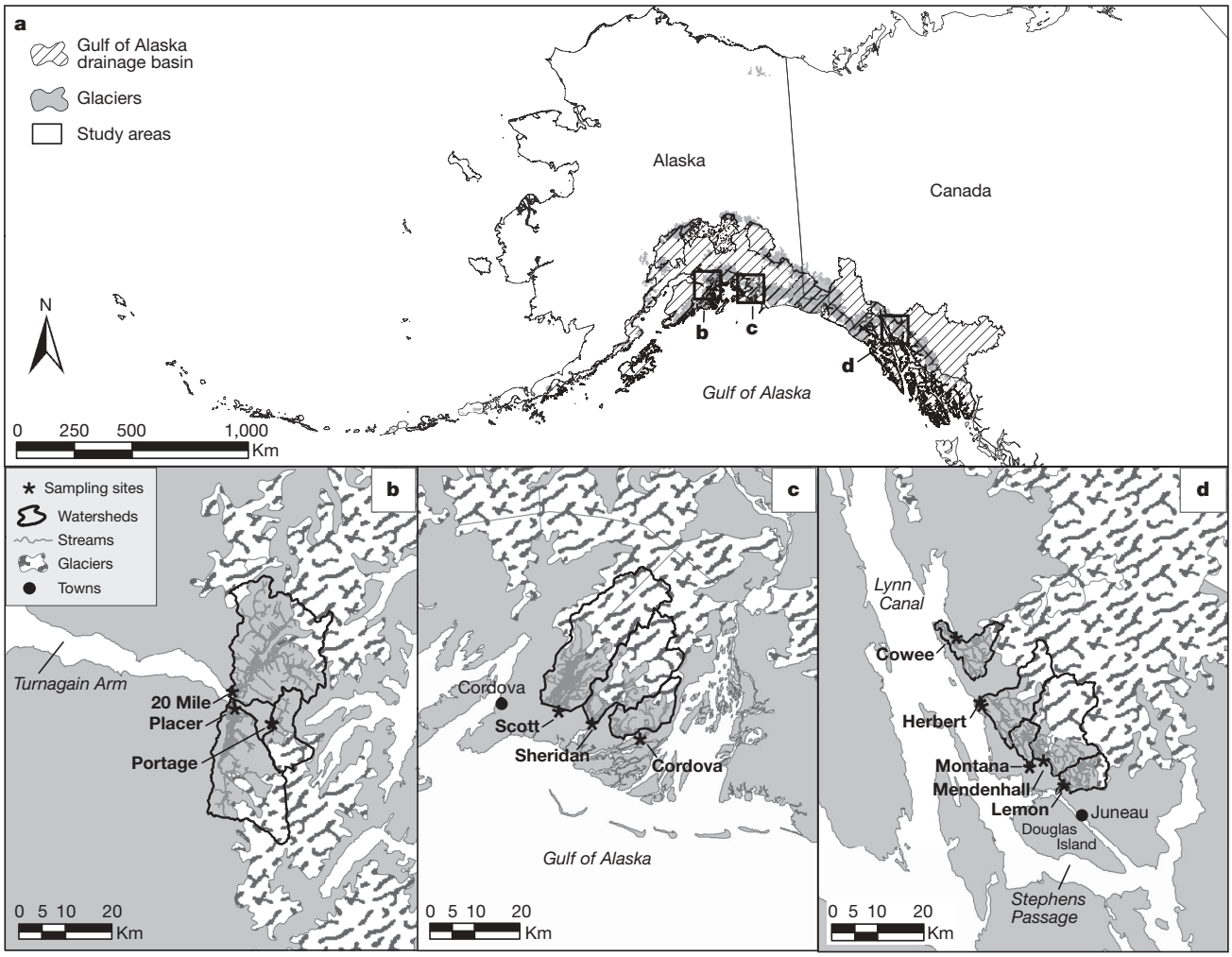

Figure 1 | Map of the Gulf of Alaska drainage area. a, The region draining into the GOA covers 420,500 km^2 within the United States and Canada and contains 75,300 km^2 of glaciers (shown in dark grey). **b–d**, Eleven watersheds (named in bold font) around the GOA were sampled within 6 km of their estuaries in three locations: Girdwood (**b**), Cordova (**c**) and Juneau (**d**). The watershed areas ranged from 37 to 430 km^2 (mean, 201; s.e., 41).

consistent with DOC derived from autochthonous material in freshwater and marine ecosystems[16,17].

Unlike $\delta^{13}C$, which is a bulk property of DOM, lignin phenols are a unique biomarker for vascular plants and thus terrigenous plant material in aquatic ecosystems[17,18]. Across the 11 watersheds, carbon-normalized lignin yields decreased dramatically with increasing watershed glacier area (Table 1; $r^2 = 0.91$, $P < 0.001$). This finding indicates that the bulk of the DOM in glacially dominated rivers is not directly derived from higher plants. The presence of abundant, active microbial communities in supra[19]-, sub[8]- and pro[20]-glacial environments, combined with limited spectroscopic observations[12] and the low C:N values[11] of DOM in glacial streams, have previously led to the hypothesis that DOM in glacial runoff has a microbial source. Our findings provide direct corroboration of this hypothesis through three independent lines of evidence, indicating that increasing glacier contributions to streamflow shift riverine DOM sources from vascular plant material toward microbial biomass.

In order to better understand the fate and impact of glacier-derived microbial DOM on coastal ecosystems, we conducted short-term (2 week) bioavailability incubations of riverine DOC with

Table 1 | Data from sample watersheds

Watershed	Glacier cover (%)	DOC (mg C l^{-1})	Protein fluor. (%)	δ^{13}C-DOC (‰)	Lignin (mg per 100 mg OC)	Bioavailable DOC (%)
Montana	0	2.2	2.7	−25.3	0.45	23
Cowee	9	1.5	4.2	−24.4	0.38	26
Cordova	16	1.4	10.1	−25.6	0.36	36
Lemon	25	1.1	23.7	−23.1	0.23	42
20 Mile	37	1.7	20.3	−24.1	0.14	31
Herbert	38	1.1	25.2	−24.5	0.25	40
Placer	48	1.4	33.9	−22.6	0.10	60
Portage	52	0.8	41.1	−24.6	0.11	48
Scott	52	1.0	55.5	−22.9	0.08	64
Mendenhall	55	0.7	39.6	−23.4	0.11	41
Sheridan	64	0.6	77.0	−22.0	0.09	66

Shown are glacier coverage, concentrations of DOC, and chemical and spectroscopic characteristics of DOC. Protein fluorescence is the relative contribution of the two DOM fluorescence components associated with proteinaceous material to the total fluorescence of the nine fluorescence components identified by our PARAFAC model as described in Methods. $\delta^{13}C$ values are expressed as per mil relative to the Pee Dee Belemnite standard, where $\delta^{13}C = [(R_{sample}/R_{standard}) - 1] \times 1{,}000$, and R is the ratio of ^{13}C to ^{12}C; replicate analyses yielded $\delta^{13}C$-DOC values with standard deviations of ±0.1‰. Lignin carbon-normalized yields are reported as the sum of three syringyl, three vanillyl and two cinnamyl phenols.

inoculums of microorganisms from downstream near-shore marine ecosystems. DOM derived from microbially based ecosystems such as Antarctic dry lakes that lack inputs from higher plants is thought to be highly labile because of low C:N ratios and low aromatic carbon content[21]. We found that the lability of riverine DOC increased dramatically with glacier coverage (Table 1), and that the bioavailability of DOC was highly correlated with Δ^{14}C-DOC values across the 11 watersheds (Fig. 2). In the most heavily glaciated watershed, Sheridan River, 66% of the riverine DOC was readily degraded by marine microbes despite having a Δ^{14}C value of −386‰ (~3,900 yr Δ^{14}C age). Heterotrophic microbes in both sub-glacial[22] and pro-glacial[20] environments have been shown to subsist on aged carbon overrun by ice during periods of glacier advance. It is additionally possible that CO_2 respired from glacially sequestered carbon may support microbial primary production in glacial ecosystems. Along the GOA, the last major cycle of glacier retreat and re-advance occurred during the Hypsithermal warm period between 7,000 and 2,500 yr BP[23]. Our data indicate that microorganisms in GOA glacial ecosystems can liberate carbon fixed during the Hypsithermal as DOC in a form that is highly bioavailable to aquatic heterotrophs. Riverine DOC in the less glacial watersheds was substantially less bioavailable despite having modern, enriched Δ^{14}C values consistent with inputs of recently fixed carbon from temperate forest soils. These findings contradict the prevalent view that the labile fraction of riverine DOC is dominated by young, lightly degraded material[2–4]. Moreover, the fact that glaciers can release ancient DOC has important implications for the interpretation of DOC age in rivers[4] and coastal oceans[24] affected by glacial runoff.

The impact of labile glacially derived DOM on heterotrophic production in GOA marine ecosystems depends on the magnitude of DOM fluxes from glaciers. A GIS (geographic information system) model of annual precipitation on the 75,300 km^2 of glaciers that drain to the GOA was used in combination with previous estimates of distributed glacier volume loss across the region[5] to calculate the annual water flux from GOA glaciers. We estimate specific discharge from GOA glaciers at 5.4 ± 0.6 m yr^{-1} (Table 2), which yields a total annual runoff of 410 ± 40 km^3 yr^{-1} that is comparable to the annual discharge of the Mississippi River[9]. Based on previous measurements of DOC concentrations in glacial runoff[12–14], we suggest that direct runoff from GOA glaciers produces a conservative DOC flux of 0.13 ± 0.01 Tg yr^{-1} to downstream ecosystems (Table 2). Furthermore, the DOC bioavailability value from the most heavily glaciated catchment (Sheridan; Table 1) suggests that ~0.1 Tg of the annual DOC derived from GOA glaciers is readily bioavailable. Because glacial streamwater turbidities are high and riverine transit times from glaciers to their estuaries are short across broad regions of the GOA, a substantial portion of this labile DOC is probably delivered to marine heterotrophic communities without biological or photochemical alteration. The biogeochemical significance of inputs of labile DOM discharged from glaciers is magnified by the relatively small volume of the GOA. On a per volume basis, the flux of labile glacier-derived DOM to the shelf waters of the GOA is approximately 25–50% of the total labile DOM input to the polar surface waters of the Arctic Ocean[25,26], which has the highest per volume inputs of DOM of any ocean on Earth[27].

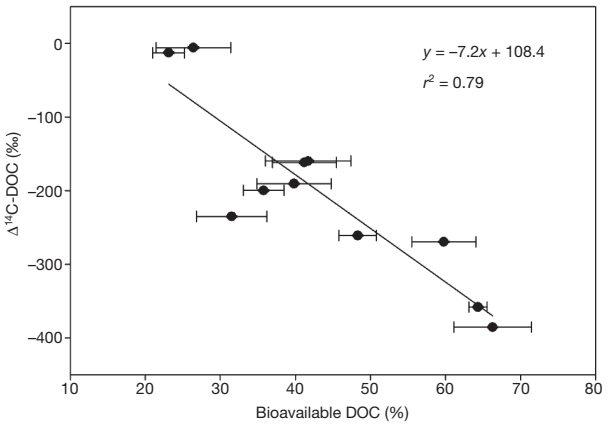

Figure 2 | Relationship between Δ^{14}C-DOC and bioavailable DOC for the 11 rivers sampled. The percentage of riverine DOC that was readily bioavailable to marine microorganisms increased significantly as Δ^{14}C-DOC values became more depleted ($y = -7.2x + 108.4$; $r^2 = 0.79$; $P = 0.001$). Values of Δ^{14}C are expressed as the deviation in per mil (‰) from the ^{14}C activity of nineteenth century wood. Errors (±1 s.d.) associated with Δ^{14}C AMS analyses averaged 2.0‰ (±20 yr for radiocarbon age) and error bars are smaller than the symbols. Error bars on bioavailable DOC are 1 s.e.

Table 2 | Total and area-weighted annual fluxes from glaciers draining into the GOA

	Water		DOC	
	(km^3 yr^{-1})	(m yr^{-1})	(10^9 kg yr^{-1})	(kg km^{-2} yr^{-1})
Glacial runoff	320 ± 30	4.2 ± 0.4	0.10 ± 0.01	1,300 ± 110
Glacial wastage	90 ± 30	1.2 ± 0.4	0.03 ± 0.01	350 ± 120
Total flux	410 ± 30	5.4 ± 0.6	0.13 ± 0.01	1,650 ± 160

Glacial runoff is the annual material flux from glaciers assuming glacier volume remains constant. Glacial wastage is the annual material flux resulting from lost glacier volume due to thinning and retreat (from ref. 5 for the period mid-1990s to 2001). The wastage of GOA glaciers generates approximately 20% of the total glacier fluxes of water and carbon.

The quantitative importance of glacial ecosystems as sources of riverine DOM has been greatly underappreciated, as evidenced by the dearth of studies on DOM dynamics in glacial rivers[12,13]. However, the annual area-weighted flux of DOC that we report for GOA glaciers (1,650 kg km^{-2} yr^{-1}; Table 2) is higher than the average per area flux of DOC from the watersheds of the five largest rivers draining to the Arctic Ocean (1,600 kg km^{-2} yr^{-1})[4]. Thus, we conclude that glacial ecosystems, which cover approximately 15,000,000 km^2 or ~10% of the Earth's surface, have the potential for substantial DOM export in a form that is highly available to aquatic heterotrophs. Along the GOA, glacier wastage accounts for a substantial portion (~20%, Table 2) of the total riverine flux of water and DOM. As a result, fluxes of glacier-derived DOM to the GOA are likely to increase in the near term as ice thinning rates[28] and discharge in glacial rivers[29] continue to rise.

Globally, the rate of glacier ice loss from terrestrial storage is increasing, with important implications for sea level[30] and the physical oceanography of coastal oceans[10]. Our findings indicate that future changes in discharge from glacial rivers may have previously unrecognized impacts on coastal biogeochemistry. Because bacterial production in coastal river plumes can be largely supported by terrigenous DOM[31], our results suggest that changes in the magnitude and timing of glacial runoff to the ocean could alter carbon availability and heterotrophic productivity in marine ecosystems. These changes could be particularly pronounced in regions that currently support commercially important fisheries such as the GOA and the North Atlantic, the latter influenced by a 41% increase in Greenland ice sheet discharge between 1961–1990 and 1998–2003[32].

Extending our estimates of glacier-derived DOM export to other regions of the world will require sampling and characterization of DOM in additional glacial rivers. Moreover, the amount and quality of organic matter within and beneath other coastal glaciers may differ from that of the coastal temperate rainforests of Alaska. Even so, our results demonstrate that glacial ecosystems are quantitatively important and highly dynamic sources of reduced carbon to freshwater and marine ecosystems that receive their runoff. The existence of such large and highly labile carbon fluxes from GOA glaciers underscores the uncertainties in carbon budgets of coastal regions, which play critical roles in moderating the flux of reactive species to the ocean.

METHODS SUMMARY

Stream samples from 11 coastal watersheds on the Gulf of Alaska were collected over a three day period in late July 2008 and were filtered within one day of

collection. Water samples were immediately analysed for bulk DOC concentration and DOM fluorescence. Protein fluorescence components were quantified from fluorescence excitation-emission matrices using the multivariate modelling technique parallel factor analysis (PARAFAC), which decomposes the fluorescence spectra of DOM into independent components. Streamwater DOM was also analysed for δ^{13}C-DOC. Lyophilized DOM samples from each site were analysed for lignin phenols and Δ^{14}C-DOC. To determine the bioavailability of DOC from the study streams, a laboratory incubation was conducted using near-shore marine water from the GOA as a microbial inoculum.

Fluxes of water from glaciers along the GOA were estimated using a combination of: (1) runoff derived from PRISM (parameter-elevation regression on independent slopes model) precipitation models that were calibrated with regional streamflow data and (2) runoff derived from the estimates of glacier wastage in ref. 5. Estimates of glacial runoff (1) and glacier wastage (2) were constrained using the regional glacier area from ref. 5 that drains to the GOA. Fluxes of DOC delivered from glaciers to downstream aquatic ecosystems were calculated using a conservative estimate of the average melt season concentration of DOC in glacial runoff in conjunction with the modelled water fluxes from glaciers along the GOA.

Full Methods and any associated references are available in the online version of the paper at www.nature.com/nature.

Received 11 March; accepted 2 October 2009.

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Acknowledgements E. Neal and K. Smikrud contributed to the GOA glacier water flux estimates and K. Smikrud also provided Fig. 1. A. Arendt provided data on glacial wastage. We thank X. Xu at the KCCAMS facility for ^{14}C analyses, and R. Dyda and B. Holmes at UC Davis for assistance with lignin and ^{13}C-DOC analyses, respectively. Funding came from the US National Science Foundation (EAR-0838587), a University of Alaska Seed Grant (to E.H.) and the USDA Forest Service, Pacific Northwest Research Station. The use of trade or firm names in this publication does not imply endorsement by the US Department of Agriculture.

Author Contributions E.H., J.F., R.G.M.S. and D.S. designed the research. J.F. performed the fieldwork and J.F., R.G.M.S. and E.H. performed laboratory analyses. P.J.H., R.E. and D.D. supported analyses and aided data interpretation. E.H. wrote the paper with substantial contributions from J.F., R.G.M.S. and P.J.H. All authors discussed the results and commented on the manuscript.

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METHODS

Sample collection and analysis. Stream samples from each of the 11 sites were collected as composites of three grab samples collected in a well-mixed region of the stream. Samples were stored on ice and returned to the University of Alaska Southeast for processing within one day of collection. Samples were filtered twice with precombusted 47-mm glass fibre filters (0.7 μm followed by 0.3 μm) to remove fine glacial silt and analysed for DOC (Shimadzu TOC-V high-temperature combustion) and DOM fluorescence (Jobin Yvon Horiba Fluoromax-3) at the USDA Forestry Science Lab in Juneau, Alaska. Fluorescence excitation-emission matrices (EEMs) were created by measuring fluorescence intensity across a range of excitation (240–450 nm) and emission (300–600 nm) wavelengths. Parallel factor analysis (PARAFAC) modelling of fluorescence EEMs was conducted with Matlab[33]. PARAFAC was used to identify and determine the relative contribution of protein fluorescence components of DOM. δ^{13}C-DOC samples were analysed at UC Davis using a Model 1010 TOC Analyser (OI Analytical) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd). Streamwater DOC from filtered samples was lyophilized using a Labconco freeze drier (FreezeZone 2.5) at −50 °C and was stored in a desiccator until analysis. Lignin phenols were analysed at UC Davis as described in ref. 18. Blank concentrations never exceeded 5% of the total lignin phenols in an individual extract. Δ^{14}C-DOC was measured at the UC Irvine KCCAMS facility and values were corrected for sample δ^{13}C. The bioavailability of DOC was determined as the difference in DOC before and after a 14-day laboratory incubation as described in ref. 33. The microbial inoculum was prepared using GOA near-shore marine water filtered through pre-combusted Whatman GF/D filter (nominal pore size 2.7 μm).

Glacial water and carbon flux estimates. Annual runoff from GOA glaciers was estimated as the sum of (1) glacier runoff, the annual water flux from glaciers assuming glacier volume remains constant, and (2) glacier wastage, the annual material flux resulting from lost glacier volume due to thinning and retreat. Glacier runoff was estimated using a GIS layer of glacier coverage in Alaska and the Yukon from ref. 5 in combination with PRISM precipitation models for Alaska, the Yukon Territory, and British Columbia (http://www.prism.oregonstate.edu/). The PRISM data are annual average precipitation data for the period 1960–1990 and are gridded at 2 km^2 (ref. 34). Precipitation data were applied to the glacier area draining to the GOA to derive runoff from glaciers. Annual precipitation on glaciers was converted to annual runoff by calibration against annual discharge from 36 watersheds that contain USGS stream gauges with more than 10 years of records. The GOA drainage basin was divided into two regions. Twenty-one USGS stream gauges in south-central and southwest Alaska (region 1) and fifteen USGS stream gauges along the central GOA coast and southeastern Alaska (region 2) were used to compute calibration factors that converted annual PRISM precipitation volumes into annual runoff volumes from glaciers in each of the two regions. The majority of the USGS gauges used to compute calibration factors were located in watersheds that contained glaciers. Because glacial wastage was calculated separately (see below), we used watershed glacier area and glacier thinning rates in ref. 5 to calculate the mean annual volume of discharge from glacier wastage in each of the calibration watersheds. Runoff from glacier wastage was then subtracted from the annual runoff from our calibration gauges in order to avoid double counting this component of glacier runoff in our estimates. Runoff errors were estimated as the standard error of the calibration factor relating PRISM precipitation to runoff in each of the two regions. Glacial wastage and associated errors were calculated using measured glacial wastage for the period mid-1990s to 2001 (ref. 5) from the portion of Alaska/Yukon glaciers that drain to the GOA.

Our glacial discharge estimates (runoff + wastage) are conservative for two reasons: (1) we found that as elevation increased, the PRISM model increasingly underestimated runoff, thus our runoff calibration factors based on watersheds that included some low elevation area probably underestimated runoff from high-elevation glaciers, and (2) recent distributed estimates of glacier wastage from southeast Alaska[28] have shown that current rates of glacial wastage are substantially higher than the estimates from ref. 5 we used. To calculate fluxes of DOC, we used a conservative estimate of the average melt season concentration of DOC in glacial runoff (0.3 mg C l^{-1}) in combination with the modelled glacier water fluxes. The [DOC] estimate we chose was based on our data and previous studies of seasonal DOC dynamics in glacier rivers[12–14]. Unlike northern rivers draining permafrost regions in which DOM is predominantly derived from terrestrial vegetation and soil organic matter[4,26,27], glacier runoff does not exhibit a pronounced spring flush or strong seasonal variability in either the concentration[13,14] or quality[12] of riverine DOM. Thus our DOC flux estimates and associated characterization of the chemical and isotopic composition of glacial DOM are consistent with the current understanding of riverine DOM outputs from glacial ecosystems.

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