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Key Points:
- Heavily glacierized watersheds can have high organic carbon yields driven largely by elevated levels of particulate organic carbon export
- Watershed glacier coverage influences the importance of C availability and hydrological transport for controlling watershed OC balances
- Glacier shrinkage will increase riverine DOC:POC yield ratios and likely alter the balance of petrogenic and biogenic POC in rivers

Supporting Information:
- Supporting Information S1

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Glacier Loss Impacts Riverine Organic Carbon Transport to the Ocean

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Abstract Lateral transport of organic carbon (OC) to the coastal ocean is an important component of the global carbon cycle because rivers transport, mineralize, and bury significant amounts of OC. Glaciers drive water and sediment export from many high-elevation and high-latitude ecosystems, yet their role in watershed OC balances is poorly understood, particularly with regard to particulate OC. Here, we evaluate seasonal water, sediment, and comprehensive OC budgets, including both dissolved and particulate forms, for three watersheds in southeast Alaska that vary in glacier coverage. We show that glacier loss will shift the dominant size fraction of riverine OC from particulate toward dissolved and potentially alter the provenance of particulate OC. Glacier coverage also controls whether OC export is source (C stock) or transport (runoff) limited at the watershed scale. These findings provide insight into the future trajectory of riverine OC export in glacierized regions.

Plain Language Summary Rivers transport large quantities of organic carbon from the land to the ocean; however, the role that glaciers play in this process is not well understood. We measured organic carbon leaving three watersheds in coastal Alaska that vary in their relative amount of glacier cover to understand how glacier shrinkage will impact the amount and type of organic carbon in rivers. We found that changes in glacier coverage will increase transport of dissolved organic carbon in rivers and decrease transport of particulate organic carbon. Sources of particulate organic carbon in rivers may also change as glaciers shrink. In watersheds, glaciers also appear to influence whether transport of OC in rivers is controlled by the availability of carbon in the watershed versus the availability of water to move that carbon. These findings provide insight into how the loss of glaciers will change the transport of organic carbon in rivers.

1. Introduction

Rivers transport ~0.4 Pg yr^{-1} of organic carbon (OC) to the ocean, with roughly equal contributions from dissolved (DOC) and particulate (POC) species (Dai et al., 2012; Galy et al., 2015). The size fraction of riverine OC is important because DOC can be rapidly metabolized and returned to the atmosphere, while POC is more likely to be deposited in marine sediments where it can be sequestered over geologic time periods. The impact of riverine OC transport on atmospheric CO_2 is influenced by the source and magnitude of lateral DOC export and the balance between delivery of modern biogenic POC to sedimentary environments and the oxidation of ancient petrogenic (rock-derived) POC from catchment bedrock (Hilton, 2017). Runoff from glaciers outside of the ice sheets (henceforth referred to as glaciers) is estimated to contribute at least 1.3 Tg yr^{-1} to riverine OC export, predominantly as POC (Hood et al., 2015; Li et al., 2018). However, the magnitude and size fraction of this estimate are extremely poorly constrained, largely because of a lack of data on POC yields from glaciers.

Globally, watershed yields of POC are tightly coupled with sediment yields and dominated by biospheric POC, which accounts for ~80% of POC export to the ocean (Galy et al., 2015). It is unclear how these findings apply to glacierized watersheds, which are characterized by high rates of physical weathering and sediment export (Hallet et al., 1996) but low rates of net primary productivity and small organic matter stocks (Anesio & Laybourn-Parry, 2012; Stibal et al., 2012). Recent studies in Greenland suggest that OC export from the ice sheet is dominated by POC (70–90%; Bhatia et al., 2013; Kohler et al., 2017; Lawson et al., 2014); however, the size fractionation of OC in runoff from glaciers may be more variable (Tockner et al., 2002) due to differences in glacier sediment production and catchment vegetation. Export of DOC from glaciers has been relatively well characterized compared to POC and appears to scale with catchment water fluxes (Hood et al., 2009, 2015; Li et al., 2018). Overall, the export of DOC and POC from glaciers appears to be decoupled (Hood et al., 2015; Kohler et al., 2017), although microbial OC production at the glacier surface may act as a source of both DOC and POC in glacier ecosystems (Andrews et al., 2018; Musilova et al., 2017; H. J. Smith et al., 2017).

Understanding how glaciers contribute to riverine OC export is critical because glaciers are expected to lose 29–41% of their 2006 volume by 2100 (Radić et al., 2014), and global glacier runoff is projected to decrease by roughly 260 $km^3\ yr^{-1}$ (~20%) over the same time period (Bliss et al., 2014). There are myriad pathways by which glacier loss can influence the source and concentration of OC in proglacial rivers including shifts in hydrology, above ground carbon stocks, and erosion rates (Moore et al., 2009). At the watershed scale, the net balance between decreased OC export from lower sediment and water yields (Milner et al., 2017) and increased mobilization of OC stocks associated with the expansion of vegetation in emergent terrestrial ecosystems (Buma & Barrett, 2015) will ultimately determine the impact of glacier loss on riverine OC budgets and rates of OC burial along glacierized coastal margins (Cui et al., 2016).

In this study, we quantified DOC and POC concentrations and export and used $\delta^{13}C$ to evaluate sources of POC from three watersheds in and adjacent to the Juneau Icefield (JIF) in the Coast Range of Alaska. The watersheds, which span a gradient of glacier coverage from 0% to 49%, were sampled at least twice weekly during May–October, a period that accounts for ~70–90% of annual discharge in these watersheds. Our aim was to assess how watershed glacierization moderates the relationship between catchment yields of water and OC and thus how glacier recession will alter: (1) the magnitude and size fractionation of OC delivered to coastal margins and (2) the source and transport processes that control lateral OC export at the catchment scale.

2. Study Sites and Methods

2.1. Study Watersheds

Streamwater samples were collected 2–3 times weekly (n = 48 for all analytes except Herbert River (HR) sediment and POC n = 44) across the full glacier melt season (May–October 2013) from three coastal watersheds adjacent to the JIF. The 3,800-km^2 JIF is experiencing high rates of ice thinning (1–5 $m\ yr^{-1}$; Berthier et al., 2018) at lower elevations and is expected to lose about two thirds of its volume by 2100 (Ziemen et al., 2016). HR watershed (152 km^2) has a mean slope of 18° and is dominated by the 75-km^2 Herbert Glacier, which is a major outlet glacier from the JIF (Figure S1, Table S1). Cowee Creek (CC) watershed (110 km^2) has two small alpine glaciers (14 km^2) in its headwaters and a mean slope of 23°. Peterson Creek (PC; 24 km^2) is a low-gradient forested watershed with abundant wetlands that contains seasonal snow but no glacier ice and has a mean slope of 12°. Annual average discharge based on 6 (HR), 9 (PC), and 11 (CC) years of data ranges from 1.3 $m^3\ s^{-1}$ (1,771 mm yr^{-1}) in PC to 10.2 $m^3\ s^{-1}$ (2,917 mm yr^{-1}) in CC and 16.7 $m^3\ s^{-1}$ (3,476 mm yr^{-1}) in HR. The three watersheds contain negligible intermittent storage for sediment and POC within the stream network and drain directly into the 140-km-long Lynn Canal fjord. Both HR and CC have forest (25% and 57%, respectively) and wetland (5%) cover in the proglacial portions of the watershed (Table S1). All three watersheds have anadromous Pacific salmon runs (*Oncorhynchus* spp.) lasting from late July through early September, with spawner densities inverse to glacier coverage (Fellman et al., 2014).

The bedrock geology of HR and CC is dominated by a foliated tonalite sill of the coast plutonic complex, which intruded into the region during the Cretaceous period. Erosion-resistant tonalite forms the high peaks of the JIF; however, there are substantial outcrops of older (Triassic to Paleozoic), potentially POC-bearing, metasedimentary, and metavolcanic rock throughout the icefield complex (Wilson et al., 2015). In both HR and CC, there are mapped lenses of carbonaceous shale, metalimestone, phyllite, and marble above the glacier termini (Wilson et al., 2015). Downstream of the glacierized areas, HR and CC are underlain by a variety of metamorphosed sedimentary and volcanic rocks of the Taku terrane, including carbonaceous slate phyllite, slate, marble, quartzite, metaturbidites, and volcanic tuff. The lower reaches are dominated by Quaternary alluvial and glaciomarine deposits. The PC watershed contains thick (commonly 2 m) layers of peat that is up to 10,000 years old overlying the Cretaceous-Jurassic greywacke and slate that dominate the underlying bedrock geology. In lower PC, where samples were taken, the substrate is composed of raised glaciomarine terraces with low permeability soils.

2.2. Chemical and Water Isotopic Analyses

Triplicate samples for DOC were filtered into precombusted (450°C for >5 h) amber glass vials through precombusted Whatman GF/F filters (0.7 μm). Duplicate POC and sediment samples were collected in 2-L polycarbonate bottles. Samples were collected from a wadable, well-mixed portion of the stream channel. Sediment and POC samples were manually depth integrated by filling the sample bottle across the depth of the stream during collection. To investigate supraglacial POC sources, we also collected five POC samples from cryoconite holes on the surface of Mendenhall Glacier, a major outlet glacier from the JIF located 20 km south of Herbert Glacier. Mendenhall was chosen because of its accessibility compared to glaciers in CC and HR.

Samples for DOC analysis were stored at 4°C and measured on a Shimadzu TOC-V CSH analyzer with a high sensitivity catalyst within 48 h of collection. The standard deviation of duplicate analyses ranged from 0.01 to 0.07 mg C/L for HR, 0.01–0.12 mg C/L for CC, and 0.01–0.28 mg C/L for PC. Samples for POC and ^{13}C-POC were analyzed on the same filters used to measure sediment. Sediment was analyzed by filtration of a known water volume onto precombusted Whatman GF/F filters (0.7 μm). Filters were then dried and reweighed to calculate sediment concentration. Differences between duplicate total suspended sediment samples averaged 0.4 mg/L for samples below 5 mg/L, 4.6 mg/L for samples from 10–100 mg/L, and 21.1 mg/L for samples greater than 100 mg/L.

Samples for δ^{13}C-DOC were analyzed on an O.I. Analytical Model 1010 TOC analyzer interfaced to a PDZ Europa 20–20 IRMS (Sercon Ltd.) following Spencer et al. (2009). Samples for POC concentration and riverine and supraglacial δ^{13}C-POC were treated to remove carbonates by a triple sulfurous acid addition (Connelly et al., 2015) and analyzed at the UC Davis Stable Isotope Facility using a Micro Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) interfaced to a PDZ Europa 20–20 IRMS (Sercon Ltd., Cheshire, UK). POC concentrations (mg C L^{-1}) were determined by dividing the elemental C mass by the volume of water that passed through the filter. Standard deviations for duplicate analyses ranged from 6 to 691 mg/C for POC and from 0.02‰ to 0.37‰ for δ^{13}C-DOC.

2.3. Hydrology

We modeled daily discharge for HR using historic U.S. Geological Survey discharge data from HR (#15054200) and Mendenhall River (MR; #15052500), which is similar in size (222 km^2), glacier cover (63%), elevation range, and aspect. The model, based on 5 years of historical daily flow in HR and MR (1966–1971), was robust across the seasonal range of discharge (HR = 0.463 MR + 56.74, r^2 = 0.93, n = 1,726). Discharge in CC was measured at 15-min intervals for the study period using a stilling well equipped with a pressure transducer (Solinst Levelogger Gold model 3001). Discharge measurements (n = 15) were made across a wide range of stage to derive the stage-discharge relationship used to calculate streamflow at CC. Discharge in Peterson Creek was measured at a stream gage maintained by the Alaska Department of Fish and Game.

2.4. Statistics and OC Flux Calculations

To evaluate catchment OC balances, the relationship between runoff (Q) and OC yields (Y) was modeled using a power function ($Y = aQ^b$), where the slope coefficient (b) refers to chemostasis ($b = 1$), source limitation ($b < 1$), or transport ($b > 1$) limitation of catchment-scale OC export (Boix Canadell et al., 2019; Zarnetske et al., 2018). For each model, we report the coefficient of determination (r^2) and p value for the linear fit in log space, and similar to previous studies, our models do not account for temporal autocorrelation in the data (Boix Canadell et al., 2019; Vaughan et al., 2017).

One way repeated measures ANOVAs with Tukey post hoc pairwise multiple comparison tests were used on log transformed data to evaluate differences in daily sediment and POC yields and δ^{13}C-POC values between sites. All statistics were calculated using Systat software. For intersite δ^{13}C-POC comparisons, samples collected during peak salmon spawning (3 weeks, six samples) were removed from the PC data set because spawning Pacific salmon contributed marine-derived POC to streamwater that is highly enriched in δ^{13}C (approximately −20‰; Chaloner et al., 2002) compared to the background watershed POC load.

Table 1
Mean Concentrations (With Range) of POC and DOC and Yields of Water, Sediment, POC, DOC, and OC From the Three Study Watersheds

	PC	CC	HR
Mean POC (mg C L^{-1})	0.8 (0.1–2.3)	0.5 (0.1–1.9)	0.7 (0.2–2.5)
Mean DOC (mg C L^{-1})	8.1 (3.5–14.6)	1.3 (0.4–5.2)	0.8 (0.2–3.5)
Runoff (mm yr^{-1})	1,900	3,231	4,224
Sediment yield (t km^{-2} yr^{-1})	4.9	65.1	964
POC yield (tC km^{-2} yr^{-1})	1.3	1.7	4.0
DOC yield (tC km^{-2} yr^{-1})	19.8	4.2	2.9
OC yield (tC km^{-2} yr^{-1})	21.1	6.0	6.9
Sediment:POC yield ratio	4	38	241

Daily DOC, POC, and sediment fluxes were calculated from the product of measured constituent concentrations and daily water fluxes. Annual constituent fluxes were calculated from the product of discharge-weighted mean concentrations and annual discharge for each watershed (Lawson et al., 2014). Daily and annual constituent yields were calculated by normalizing fluxes to watershed area.

3. Glacier Influence on Riverine OC

3.1. OC Release From Glaciers

Mean concentrations of POC during the runoff season were similar between watersheds (0.5–0.8 mg C L^{-1}), while daily concentrations ranged from 0.1 to 2.5 mg C L^{-1} (Table 1). In heavily glacierized HR, concentrations of POC were higher in the first half of the melt season and decreased by an average of 66% after mid-August (Figure S2). There was no seasonal pattern in POC in CC, while in PC, the highest POC concentrations occurred during salmon spawning in August and early September, likely as a result of bioturbation (Moore et al., 2007). Mean concentrations of DOC were similar to POC in HR but substantially higher and more variable compared to POC in CC and PC (Table 1; Figure S2).

Catchment water yields increased with glacierization to >4 m yr^{-1} in HR (Tables 1 and S2). Across the watershed gradient, differences in OC concentrations and water yields resulted in POC yields increasing by ~3 times and DOC yields decreasing by ~7 times between forested PC and heavily glacierized HR (Tables 1 and S2). In the glacierized catchments, the total OC yield was higher in HR because the decrease in POC yield as glacier coverage decreased between HR and CC was larger than the increase in DOC yield associated with the higher forest coverage in CC. Forested PC had the highest OC yield consistent with high levels of DOC export from coastal temperate rainforest watersheds (Oliver et al., 2017) compared to glaciated watersheds with low vegetation coverage and poorly developed soils (Hood & Scott, 2008). There are few comprehensive OC budgets from glacierized watersheds for comparison; however, the OC yield from HR had a similar OC size fraction ratio (DOC:POC) but was nearly an order of magnitude larger than the annual OC yield from the glacierized Val Roseg Catchment in Switzerland (7.6 kg ha^{-1} yr^{-1} with 53% as POC; Tockner et al., 2002).

Globally, small mountain rivers (<5,000 km^2) have the highest rates of POC delivery to the ocean (Hilton et al., 2008) and thus provide a benchmark against which to evaluate the relative importance of glaciers as a source of riverine POC. The POC yield from heavily glacierized HR is lower than all but two annual POC yields from a compilation of 38 mountain rivers from tropical, temperate, and boreal/arctic ecosystem and equates to 18% of the median POC yield (22 tC km^2 yr^{-1}) from these watersheds (Hilton, 2017). However, OC yields from HR are higher than the median POC (3.4 tC km^2 yr^{-1}) and DOC (2.3 tC km^2 yr^{-1}) yields from 13 coastal, mountainous watersheds in New Zealand that drain areas of temperate rainforest similar to southeast Alaska (Carey et al., 2005). The HR watershed is one of tens of heavily glacierized catchments that drain into Lynn Canal, the longest and deepest fjord in North America. The large POC yields we document from HR support the hypothesis that glacier runoff contributes to OC burial within glacierized fjords in coastal Alaska (Cui et al., 2016), rates of which are >100 times the global ocean average (R. W. Smith et al., 2015). More generally, the fact that POC yields from HR are comparable to at least the low end of reported POC yields from mountain rivers highlights the importance of glaciers for land-to-ocean transport of POC along glacierized coastal margins.

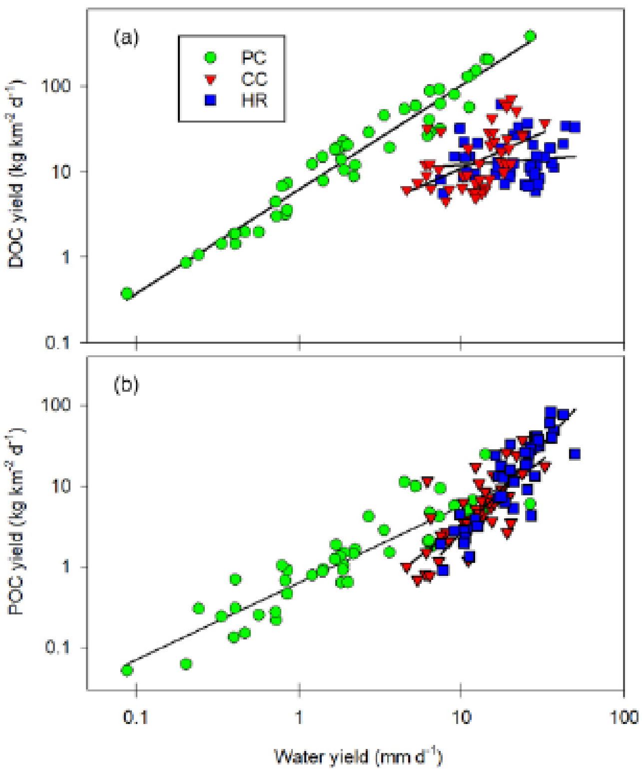

Figure 1. Relationship between daily water yields (Y_{wat}) and daily yields of DOC (Y_{DOC}; panel a) and POC (Y_{POC}; panel b). The regression lines for DOC yields are as follows: $Y_{DOC} = 6.18\ Y_{wat}^{1.217}$, $r^2 = 0.95$, $p < 0.001$ (PC); $Y_{DOC} = 1.60\ Y_{wat}^{0.837}$, $r^2 = 0.24$, $p < 0.001$ (CC); $Y_{DOC} = 8.76\ Y_{wat}^{0.139}$, $r^2 = 0.01$, $p = 0.42$ (HR). The regression lines for POC yields are as follows: $Y_{POC} = 0.64\ Y_{wat}^{0.953}$, $r^2 = 0.82$, $p < 0.001$ (PC); $Y_{POC} = 0.09\ Y_{wat}^{1.576}$, $r^2 = 0.56$, $p < 0.001$ (CC); $Y_{POC} = 0.02\ Y_{wat}^{2.174}$, $r^2 = 0.78$, $p < 0.001$ (HR). Data provided in Table S2.

3.2. Linking Water, Sediment, and OC

Runoff is a first-order driver of DOC and POC yields at the watershed scale (Hilton, 2017; Raymond & Saiers, 2010). Daily catchment water yields were significantly related to DOC yields by a power law in two of the three study watersheds (PC and CC), with the strength and slope of the relationship inverse to watershed glacierization (Figure 1a). In the glacierized watersheds, the slope coefficients (*b*) for the power law relationship between daily runoff and DOC yields were <1 (Figure 1a) indicating that DOC export is source limited. Glacierized watersheds in the Alps have been shown to be in chemostasis with regard to DOC yields (Boix Canadell et al., 2019). Our finding of source-limited DOC yields in HR and CC reflects that DOC mobilization from englacial stores (Hood et al., 2015; Li et al., 2018) and the solubilization of OC produced in supraglacial and subglacial environments (Spencer et al., 2014) does not increase proportionally with discharge. In the forested PC watershed, *b* was >1 (Figure 1a), indicating that DOC export is transport limited similar to a majority of forested watersheds across the contiguous United States (Zarnetske et al., 2018). Across the watershed sequence, the shift from source limitation to transport limitation with decreasing glacier ice was reflected in annual DOC export efficiency (kg DOC per mm runoff), which increased sharply from 104 in HR to 143 in CC and 250 in PC.

Daily water yields were significantly related to POC yields via power laws in all three watersheds, although the nature of the relationship was different than for DOC. The strength of the relationship between water and POC yields was not related to glacierization and was lowest in the mixed land cover CC watershed (Figure 1b). In the glacierized watersheds, the slope coefficients (*b*) for the power law relationship between daily runoff and POC yields were >1 (Figure 1b) indicating that POC export is transport limited such that increases in discharge mobilize new POC sources in these watersheds. In forested PC, *b* was <1 indicating that the mobilization of POC from autochthonous and allochthonous sources does not keep pace with discharge.

The changes in the efficiency of POC export across the three watersheds cannot be explained by slope as in other small mountain watersheds where erosional processes act more strongly in steeper basins (Hilton, 2017; Hilton et al., 2012). For example, POC:water yield ratios were roughly three times higher in HR (18° slope) compared to CC (23° slope). Instead, the catchment-level differences in POC export suggest that the presence and extent of watershed glacier coverage plays a role in riverine POC loss through its influence on catchment sediment yields, which increased significantly with glacier coverage (Figure 2a). POC yields also increased significantly with glacier coverage (Figure 2b), although at a much lower rate as illustrated by the ~11 times increase in median daily POC yield between PC and HR compared to the >750 times increase in median daily sediment yield between PC and HR.

Daily yields of sediment and POC were significantly positively correlated in all three watersheds, as has been shown in other mountain watersheds (Galy et al., 2015; Hilton et al., 2011), with the highest daily sediment and POC yields occurring in heavily glacierized HR (Figure S3; Table S2). The decrease in the strength of the sediment:POC yield relationship with increasing glacier coverage suggests that inputs of glacier-derived sediment may impact the extent to which sediment and POC export are coupled. Several lines of evidence suggest that glacier erosion of OC-bearing bedrock in HR and, to a lesser extent, CC may liberate petrogenic POC and contribute to the relatively high levels of POC export seen in these watersheds. The annual sediment:POC yield ratio (t sediment/t POC) decreased with glacier coverage across the watershed sequence from 241 in HR to 38 in CC to 4 in PC (Table 1). In a global survey of forested mountain rivers (Hilton, 2017), catchments where more than half of annual POC export

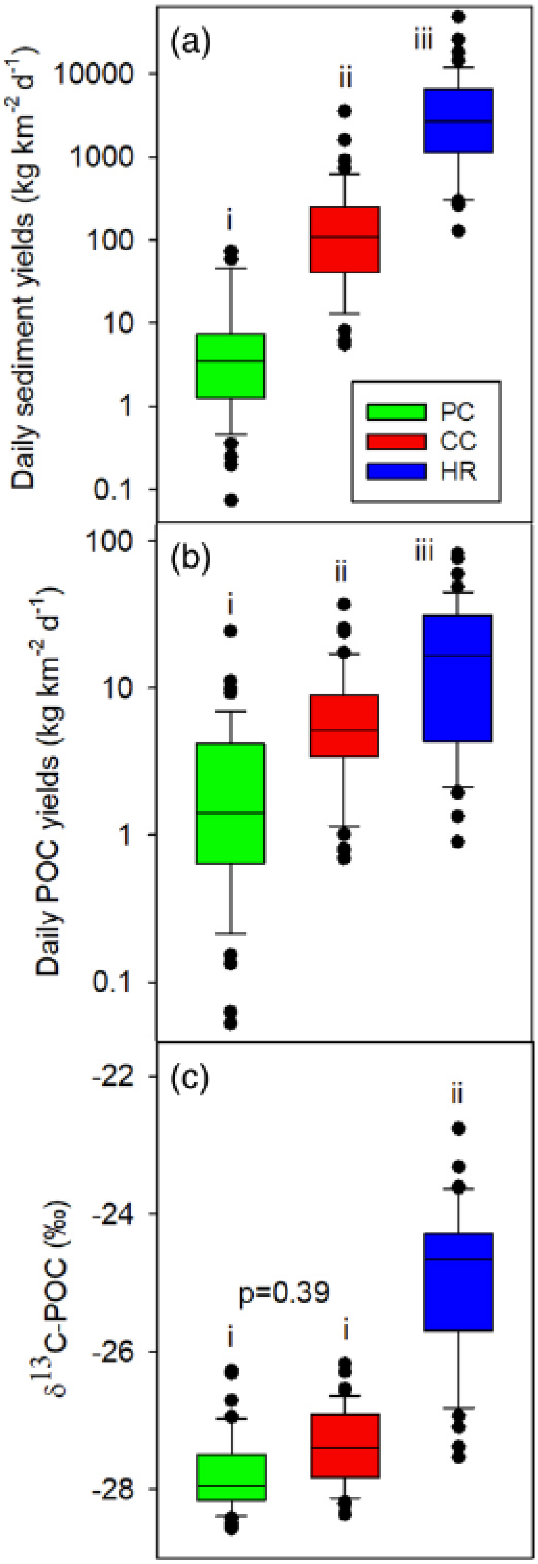

Figure 2. Box plots of daily sediment (a) and POC (b) yields and daily δ^{13}C-POC (c) for the three study watersheds. Significant differences between watersheds at $p < 0.001$, based on Tukey post hoc multiple comparison tests, are marked by roman numerals. Data are provided in Table S2.

was rock-derived had a median sediment:POC yield ratio of 270 (range 166–382, n = 15), while watersheds where more the half of annual POC export was from biogenic sources had a median sediment:POC yield ratio of only 89 (range 8–432, n = 17). Given the presence of POC-bearing rock in our study watersheds, the elevated sediment: POC yield ratio in HR would be consistent with a substantial proportion of petrogenic POC in streamwater, while the lower sediment: POC ratios in more forested CC and PC are consistent with relatively higher biogenic POC loads.

The source of riverine POC also changed across the watershed sequence as indicated by the enrichment in the carbon isotopic composition of POC (δ^{13}C-POC) with increasing watershed glacier coverage (Figure 2c). In nonglacial PC, the depleted average δ^{13}C-POC (−27.6‰) and low sediment yields are consistent with a predominance of biospheric POC derived from recently fixed carbon in C3 plant biomass (Hilton, 2017; Hilton et al., 2010). Interestingly, the mean δ^{13}C-POC value in CC was not significantly different from PC, which suggests the transition from a valley bottom glacier (HR) to the high-elevation alpine glaciers found in CC effects a substantial shift in POC provenance toward biogenic sources. In heavily glacierized HR, the average δ^{13}C-POC (−25.0‰) is on the low end of values reported for fossil POC in small mountainous rivers (−19 to −25‰; Hilton et al., 2010) and is consistent with other glacier rivers in Alaska, which are similarly enriched in δ^{13}C-POC (Walinsky et al., 2009) and strongly depleted in Δ^{14}C-POC (Arimitsu et al., 2018). The supraglacial POC samples we collected from nearby Mendenhall Glacier were relatively depleted in δ^{13}C (mean = −27.22‰, range = −26.25‰ to −28.5‰), which does not preclude supraglacial OM as a source of riverine POC in HR. The lack of δ^{13}C-POC data from bedrock within our study catchments precludes definitively linking the enriched δ^{13}C-POC signatures in HR and CC to glacier-derived petrogenic POC. However, continental shelf sediments downstream of our study watersheds contain a substantial fraction (25–50%) of old terrestrial organic matter (fraction modern = 0.1–0.68; Cui et al., 2016; Walinsky et al., 2009), which would be consistent with the glacier-mediated delivery and burial of petrogenic POC along this heavily glacierized coastal margin.

The high erosion rates associated with fast moving valley glaciers such as HR (10–100 mm yr^{-1}; Hallet et al., 1996) suggest that glaciers could function similarly to bedrock landslides by extending the "erosion depth" within the subglacial reach of the catchment (Hilton, 2017). Controls on POC loss from glacier watersheds are fundamentally different from other small mountain watersheds where the processes of POC mobilization and transport are coupled via fluvial hillslope erosion. In glaciers, these processes are decoupled because meltwater generation is a supraglacial process, while POC production depends largely on subglacial erosion (Hodson et al., 2008). The seasonal development of the englacial and subglacial hydrological system links the surface and bed thereby facilitating fluvial POC export. The efficiency of this process changes as the drainage network evolves from distributed to channelized and more efficiently evacuates sediment from previously isolated areas of the bed (Kohler et al., 2017; Swift et al., 2002). Ultimately, the link between sediment and POC export in glacierized watersheds will depend on the spatial extent of POC-bearing rocks exposed to glacier erosion.

3.3. Glacier Loss and Riverine OC Dynamics

As watershed glacierization decreases, the mechanism by which climate regulates riverine OC export shifts from the energy balance at the glacier surface to the delivery of precipitation onto catchment hillslopes. Our findings highlight that the flowpaths associated with glacier and hillslope runoff entrain very different OC sources with implications for the relative balance of DOC and POC exported in streamwater. In heavily glacierized HR, the annual DOC:POC yield ratio was <1, indicating that POC was the dominant form of OC in streamwater. The annual DOC:POC ratio increased to 2.5 in CC and to 14.6 in the forested PC catchment, where >90% of the OC exported in streamwater was DOC. An important caveat is that the predominance of DOC in the OC budget for Peterson Creek does not represent a future endpoint for larger glacier rivers in coastal Alaska; however, it is indicative of the trajectory of riverine OC size fractionation associated with glacier loss and resulting forest expansion.

From an ecosystem perspective, glacier-driven shifts in OC export from coastal watersheds will impact stocks of biolabile OC that can be incorporated into freshwater (Fellman et al., 2015) and marine (Arimitsu et al., 2018) food webs. In the case of DOC, our findings suggest that decreasing glacier coverage is likely to increase riverine yields (Boix Canadell et al., 2019). At the same time, the loss of glacier runoff will decrease the overall bioavailability of the riverine DOC pool (Hood et al., 2009; Singer et al., 2012). For POC, our findings suggest that glacier shrinkage will decrease riverine yields and potentially increase the proportion of POC derived from biogenic versus petrogenic sources (Cui et al., 2016).

Changes in glacier coverage may also indirectly impact catchment OC export through the production and mobilization of suspended sediment. The high sediment yields observed in glacier-dominated catchments (200–200,000 t km^{-2} yr^{-2}; Hallet et al., 1996) may play a role in preventing the oxidation of riverine POC because increased sedimentation is positively associated with OC burial and preservation in depositional environments (Canfield, 1994; Galy et al., 2015). In the case of HR and other heavily glacierized watersheds in the Alaska Coast Mountains, glacier-mediated production and export of clastic sediments have the potential to limit oxidation and enhance burial of both fossil and biogenic POC in receiving fjords. The burial of biogenic POC, which is derived from net primary production, represents a net sequestration of atmospheric C, while the oxidation of petrogenic POC represents a net source of C to the atmosphere. The impact of glacier-derived sediment on biogenic POC burial should peak at an intermediate level of catchment glacier coverage because it is dependent on the balance between the export of sediment produced by subglacial erosion, which decreases with glacier shrinkage (Koppes et al., 2015), and biogenic POC inputs from proglacial landscapes, which increase with glacier loss.

In coming decades, climate-driven shifts in runoff and erosion from glacierized watersheds are projected to be substantial (e.g., Bliss et al., 2014; Milner et al., 2017). Our findings indicate that changes in water and sediment yields associated with glacier loss have important implications for watershed OC budgets. We suggest that climate warming may result in greater changes in the magnitude and size fractionation of riverine OC in glacier watersheds compared to mountain watersheds that do not contain glaciers. The impact of glacier loss on riverine OC budgets will ultimately depend on the temporal synchronicity between changes in glacier runoff resulting from ice loss and shifts in land cover and catchment erosion rates, both of which are strongly impacted by the extent of glacier coverage within a watershed. Improving our understanding of how OC is generated and released in glacierized watersheds will allow us to better estimate how future shifts in riverine OC losses from glacierized watersheds will influence coastal marine OC budgets and the atmospheric CO_2 reservoir.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All data in this study are available online (https://knb.ecoinformatics.org/view/doi:10.5063/F10P0XDW). Data presented in the paper are provided in Table S2.

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References

Andrews, M. G., Jacobson, A. D., Osburn, M. R., & Flynn, T. M. (2018). Dissolved carbon dynamics in meltwaters from the Russell Glacier, Greenland Ice Sheet. *Journal of Geophysical Research: Biogeosciences*, *123*, 2922–2940. https://doi.org/10.1029/2018JG004458

Anesio, A. M., & Laybourn-Parry, J. (2012). Glaciers and ice sheets as a biome. *Trends in Ecology & Evolution*, *27*(4), 219–225. https://doi.org/10.1016/j.tree.2011.09.012

Arimitsu, M. L., Hobson, K. A., Webber, D. N., Piatt, J. F., Hood, E. W., & Fellman, J. B. (2018). Tracing biogeochemical subsidies from glacier runoff into Alaska's coastal marine food webs. *Global Change Biology*, *24*(1), 387–398. https://doi.org/10.1111/gcb.13875

Berthier, E., Larsen, C., Durkin, W. J., Willis, M. J., & Pritchard, M. E. (2018). Brief communication: Unabated wastage of the Juneau and Stikine icefields (southeast Alaska) in the early 21st century. *The Cryosphere*, *12*(4), 1523–1530. https://doi.org/10.5194/tc-12-1523-2018

Bhatia, M. P., Das, S. B., Xu, L., Charette, M. A., Wadham, J. L., & Kujawinski, E. B. (2013). Organic carbon export from the Greenland ice sheet. *Geochimica et Cosmochimica Acta*, *109*, 329–344. https://doi.org/10.1016/j.gca.2013.02.006

Bliss, A., Hock, R., & Radić, V. (2014). Global response of glacier runoff to twenty-first century climate change. *Journal of Geophysical Research: Earth Surface*, *119*, 717–730. https://doi.org/10.1002/2013JF002931

Boix Canadell, M., Escoffier, N., Ulseth, A. J., Lane, S. N., & Battin, T. J. (2019). Alpine glacier shrinkage drives shift in dissolved organic carbon export from quasi-chemostasis to transport limitation. *Geophysical Research Letters*, *46*, 8872–8881. https://doi.org/10.1029/2019GL083424

Buma, B., & Barrett, T. M. (2015). Spatial and topographic trends in forest expansion and biomass change, from regional to local scales. *Global Change Biology*, *21*(9), 3445–3454. https://doi.org/10.1111/gcb.12915

Canfield, D. E. (1994). Factors influencing organic carbon preservation in marine sediments. *Chemical Geology*, *114*(3–4), 315–329. https://doi.org/10.1016/0009-2541(94)90061-2

Carey, A. E., Gardner, C., Goldsmith, S., Lyons, W. B., & Hicks, D. M. (2005). Organic carbon yields from small, mountainous rivers, New Zealand. *Geophysical Research Letters*, *32*, L15404. https://doi.org/10.1029/2005GL023159

Chaloner, D. T., Martin, K. M., Wipfli, M. S., Ostrom, P. H., & Lamberti, G. A. (2002). Marine carbon and nitrogen in southeastern Alaska stream food webs: Evidence from artificial and natural streams. *Canadian Journal of Fisheries and Aquatic Sciences*, *59*(8), 1257–1265. https://doi.org/10.1139/f02-084

Connelly, T., McClelland, J., Crump, B., Kellogg, C., & Dunton, K. (2015). Seasonal changes in quantity and composition of suspended particulate organic matter in lagoons of the Alaskan Beaufort Sea. *Marine Ecology Progress Series*, *527*, 31–45. https://doi.org/10.3354/meps11207

Cui, X., Bianchi, T. S., Jaeger, J. M., & Smith, R. W. (2016). Biospheric and petrogenic organic carbon flux along southeast Alaska. *Earth and Planetary Science Letters*, *452*, 238–246. https://doi.org/10.1016/j.epsl.2016.08.002

Dai, M., Yin, Z., Meng, F., Liu, Q., & Cai, W.-J. (2012). Spatial distribution of riverine DOC inputs to the ocean: An updated global synthesis. *Current Opinion in Environmental Sustainability*, *4*(2), 170–178. https://doi.org/10.1016/j.cosust.2012.03.003

Fellman, J. B., Hood, E., Raymond, P. A., Hudson, J., Bozeman, M., & Arimitsu, M. (2015). Evidence for the assimilation of ancient glacier organic carbon in a proglacial stream food web: Assimilation of glacier organic carbon. *Limnology and Oceanography*, *60*(4), 1118–1128. https://doi.org/10.1002/lno.10088

Fellman, J. B., Hood, E., Spencer, R. G. M., Stubbins, A., & Raymond, P. A. (2014). Watershed glacier coverage influences dissolved organic matter biogeochemistry in coastal watersheds of southeast Alaska. *Ecosystems*, *17*(6), 1014–1025. https://doi.org/10.1007/s10021-014-9777-1

Galy, V., Peucker-Ehrenbrink, B., & Eglinton, T. (2015). Global carbon export from the terrestrial biosphere controlled by erosion. *Nature*, *521*(7551), 204–207. https://doi.org/10.1038/nature14400

Hallet, B., Hunter, L., & Bogen, J. (1996). Rates of erosion and sediment evacuation by glaciers: A review of field data and their implications. *Global and Planetary Change*, *12*(1–4), 213–235. https://doi.org/10.1016/0921-8181(95)00021-6

Hilton, R. G. (2017). Climate regulates the erosional carbon export from the terrestrial biosphere. *Geomorphology*, *277*, 118–132. https://doi.org/10.1016/j.geomorph.2016.03.028

Hilton, R. G., Galy, A., & Hovius, N. (2008). Riverine particulate organic carbon from an active mountain belt: Importance of landslides. *Global Biogeochemical Cycles*, *22*, GB1017. https://doi.org/10.1029/2006GB002905

Hilton, R. G., Galy, A., Hovius, N., Horng, M.-J., & Chen, H. (2010). The isotopic composition of particulate organic carbon in mountain rivers of Taiwan. *Geochimica et Cosmochimica Acta*, *74*(11), 3164–3181. https://doi.org/10.1016/j.gca.2010.03.004

Hilton, R. G., Galy, A., Hovius, N., Horng, M.-J., & Chen, H. (2011). Efficient transport of fossil organic carbon to the ocean by steep mountain rivers: An orogenic carbon sequestration mechanism. *Geology*, *39*(1), 71–74. https://doi.org/10.1130/G31352.1

Hilton, R. G., Galy, A., Hovius, N., Kao, S.-J., Horng, M.-J., & Chen, H. (2012). Climatic and geomorphic controls on the erosion of terrestrial biomass from subtropical mountain forest. *Global Biogeochemical Cycles*, *26*, 2012GB004314. https://doi.org/10.1029/2012GB004314

Hodson, A., Anesio, A. M., Tranter, M., Fountain, A., Osborn, M., Priscu, J., et al. (2008). Glacial ecosystems. *Ecological Monographs*, *78*(1), 41–67. https://doi.org/10.1890/07-0187.1

Hood, E., Battin, T. J., Fellman, J., O'Neel, S., & Spencer, R. G. M. (2015). Storage and release of organic carbon from glaciers and ice sheets. *Nature Geoscience*, *8*(2), 91–96. https://doi.org/10.1038/ngeo2331

Hood, E., Fellman, J., Spencer, R. G. M., Hernes, P. J., Edwards, R., D'Amore, D., & Scott, D. (2009). Glaciers as a source of ancient and labile organic matter to the marine environment. *Nature*, *462*(7276), 1044–1047. https://doi.org/10.1038/nature08580

Hood, E., & Scott, D. (2008). Riverine organic matter and nutrients in southeast Alaska affected by glacial coverage. *Nature Geoscience*, *1*(9), 583–587. https://doi.org/10.1038/ngeo280

Kohler, T. J., Žárský, J. D., Yde, J. C., Lamarche-Gagnon, G., Hawkings, J. R., Tedstone, A. J., et al. (2017). Carbon dating reveals a seasonal progression in the source of particulate organic carbon exported from the Greenland ice sheet: Trends in exported subglacial carbon age. *Geophysical Research Letters*, *44*, 6209–6217. https://doi.org/10.1002/2017GL073219

Koppes, M., Hallet, B., Rignot, E., Mouginot, J., Wellner, J. S., & Boldt, K. (2015). Observed latitudinal variations in erosion as a function of glacier dynamics. *Nature*, *526*(7571), 100–103. https://doi.org/10.1038/nature15385

Lawson, E. C., Wadham, J. L., Tranter, M., Stibal, M., Lis, G. P., Butler, C. E. H., et al. (2014). Greenland ice sheet exports labile organic carbon to the Arctic oceans. *Biogeosciences*, *11*(14), 4015–4028. https://doi.org/10.5194/bg-11-4015-2014

Li, X., Ding, Y., Xu, J., He, X., Han, T., Kang, S., et al. (2018). Importance of mountain glaciers as a source of dissolved organic carbon. *Journal of Geophysical Research: Earth Surface*, *123*, 2123–2134. https://doi.org/10.1029/2017JF004333

Milner, A. M., Khamis, K., Battin, T. J., Brittain, J. E., Barrand, N. E., Füreder, L., et al. (2017). Glacier shrinkage driving global changes in downstream systems. *Proceedings of the National Academy of Sciences*, *114*(37), 9770–9778. https://doi.org/10.1073/pnas.1619807114

Moore, J. W., Schindler, D. E., Carter, J. L., Fox, J., Griffiths, J., & Holtgrieve, G. W. (2007). Biotic control of stream fluxes: Spawning salmon drive nutrient and matter export. *Ecology*, *88*(5), 1278–1291. https://doi.org/10.1890/06-0782

Moore, R. D., Fleming, S. W., Menounos, B., Wheate, R., Fountain, A., Stahl, K., et al. (2009). Glacier change in western North America: Influences on hydrology, geomorphic hazards and water quality. *Hydrological Processes*, *23*(1), 42–61. https://doi.org/10.1002/hyp.7162

Musilova, M., Tranter, M., Wadham, J., Telling, J., Tedstone, A., & Anesio, A. M. (2017). Microbially driven export of labile organic carbon from the Greenland ice sheet. *Nature Geoscience*, *10*(5), 360–365. https://doi.org/10.1038/ngeo2920

Oliver, A. A., Tank, S. E., Giesbrecht, I., Korver, M. C., Floyd, W. C., Sanborn, P., et al. (2017). A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia. *Biogeosciences*, *14*(15), 3743–3762. https://doi.org/10.5194/bg-14-3743-2017

Radić, V., Bliss, A., Beedlow, A. C., Hock, R., Miles, E., & Cogley, J. G. (2014). Regional and global projections of twenty-first century glacier mass changes in response to climate scenarios from global climate models. *Climate Dynamics*, *42*(1–2), 37–58. https://doi.org/10.1007/s00382-013-1719-7

Raymond, P. A., & Saiers, J. E. (2010). Event controlled DOC export from forested watersheds. *Biogeochemistry*, *100*(1–3), 197–209. https://doi.org/10.1007/s10533-010-9416-7

Singer, G. A., Fasching, C., Wilhelm, L., Niggemann, J., Steier, P., Dittmar, T., & Battin, T. J. (2012). Biogeochemically diverse organic matter in alpine glaciers and its downstream fate. *Nature Geoscience*, *5*(10), 710–714. https://doi.org/10.1038/ngeo1581

Smith, H. J., Foster, R. A., McKnight, D. M., Lisle, J. T., Littmann, S., Kuypers, M. M. M., & Foreman, C. M. (2017). Microbial formation of labile organic carbon in Antarctic glacial environments. *Nature Geoscience*, *10*(5), 356–359. https://doi.org/10.1038/ngeo2925

Smith, R. W., Bianchi, T. S., Allison, M., Savage, C., & Galy, V. (2015). High rates of organic carbon burial in fjord sediments globally. *Nature Geoscience*, *8*(6), 450–453. https://doi.org/10.1038/ngeo2421

Spencer, R. G. M., Stubbins, A., Hernes, P. J., Baker, A., Mopper, K., Aufdenkampe, A. K., et al. (2009). Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. *Journal of Geophysical Research*, *114*, G03010. https://doi.org/10.1029/2009JG000968

Spencer, R. G. M., Vermilyea, A., Fellman, J., Raymond, P., Stubbins, A., Scott, D., & Hood, E. (2014). Seasonal variability of organic matter composition in an Alaskan glacier outflow: Insights into glacier carbon sources. *Environmental Research Letters*, *9*(5), 055005. https://doi.org/10.1088/1748-9326/9/5/055005

Stibal, M., Šabacká, M., & Žárský, J. (2012). Biological processes on glacier and ice sheet surfaces. *Nature Geoscience*, *5*(11), 771–774. https://doi.org/10.1038/ngeo1611

Swift, D. A., Nienow, P. W., Spedding, N., & Hoey, T. B. (2002). Geomorphic implications of subglacial drainage configuration: Rates of basal sediment evacuation controlled by seasonal drainage system evolution. *Sedimentary Geology*, *149*(1–3), 5–19. https://doi.org/10.1016/S0037-0738(01)00241-X

Tockner, K., Malard, F., Uehlinger, U., & Ward, J. V. (2002). Nutrients and organic matter in a glacial river-floodplain system (Val Roseg, Switzerland). *Limnology and Oceanography*, *47*(1), 266–277. https://doi.org/10.4319/lo.2002.47.1.0266

Vaughan, M. C. H., Bowden, W. B., Shanley, J. B., Vermilyea, A., Sleeper, R., Gold, A. J., et al. (2017). High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. *Water Resources Research*, *53*, 5345–5363. https://doi.org/10.1002/2017WR020491

Walinsky, S. E., Prahl, F. G., Mix, A. C., Finney, B. P., Jaeger, J. M., & Rosen, G. P. (2009). Distribution and composition of organic matter in surface sediments of coastal Southeast Alaska. *Continental Shelf Research*, *29*(13), 1565–1579. https://doi.org/10.1016/j.csr.2009.04.006

Wilson, F. H., Hults, C. P., Mull, C. G., & Karl, S. M. (2015). *Geologic map of Alaska* (U.S. Geological Survey Scientific Investigations No. 3340) (p. 197). https://doi.org/10.3133/sim3340

Zarnetske, J. P., Bouda, M., Abbott, B. W., Saiers, J., & Raymond, P. A. (2018). Generality of hydrologic transport limitation of watershed organic carbon flux across ecoregions of the United States. *Geophysical Research Letters*, *45*, 11,702–11,711. https://doi.org/10.1029/2018GL080005

Ziemen, F. A., Hock, R., Aschwanden, A., Khroulev, C., Kienholz, C., Melkonian, A., & Zhang, J. (2016). Modeling the evolution of the Juneau Icefield between 1971 and 2100 using the parallel ice sheet model (PISM). *Journal of Glaciology*, *62*(231), 199–214. https://doi.org/10.1017/jog.2016.13