Proglacial freshwaters are significant and previously unrecognized sinks of atmospheric CO₂

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Carbon dioxide (CO₂) emissions from freshwater ecosystems are almost universally predicted to increase with climate warming. Glacier-fed rivers and lakes, however, differ critically from those in nonglacierized catchments in that they receive little terrestrial input of organic matter for decomposition and CO₂ production, and transport large quantities of easily mobilized comminuted sediments available for carbonate and silicate weathering reactions that can consume atmospheric CO₂. We used a whole-watershed approach, integrating concepts from glaciology and limnology, to conclusively show that certain glacier-fed freshwater ecosystems are important and previously overlooked annual CO₂ sinks due to the overwhelming influence of these weathering reactions. Using the glacialized Lake Hazen watershed (Nunavut, Canada, 82°N) as a model system, we found that weathering reactions in the glacial rivers actively consumed CO₂ up to 42 km downstream of glaciers, and cumulatively transformed the High Arctic’s most voluminous lake into an important CO₂ sink. In conjunction with data collected at other proglacial freshwater sites in Greenland and the Canadian Rockies, we suggest that CO₂ consumption in proglacial freshwaters due to glacial melt-enhanced weathering is likely a globally relevant phenomenon, with potentially important implications for regional annual carbon budgets in glacialized watersheds.

M o s t inland freshwater systems, such as lakes, rivers, ponds, and reservoirs, are net emitters of CO₂ to the atmosphere on an annual basis (1). Biological and abiotic processes leading to CO₂ supersaturation and resultant emissions from surface waters include net heterotrophy (2), catchment inputs of dissolved inorganic carbon (DIC) (3, 4), photochemical mineralization of organic matter (5, 6), and calcite precipitation (7). Glacier-fed rivers and lakes have hitherto been overlooked in studies of CO₂ cycling, despite their rapid expansion after enhanced glacier melt (8, 9). CO₂ cycling in glacialized watersheds differs critically from what is observed in other northern, temperate, and tropical systems due to both little export of organic carbon (OC) from sparsely vegetated landscapes, an important subsidy of heterotrophy (2, 10), and an abundance of freshly eroded and reactive sediments susceptible to rapid chemical weathering. Together, these characteristics mean that chemical weathering controls on CO₂ fluxes in glacier-fed freshwaters could overwhelm the typical biological and abiotic processes that dominate in most nonglacierized watersheds.

Subglacial chemical weathering has been described extensively (e.g., refs. 11 to 13), but comparatively little is known about the extent of such weathering in proglacial freshwaters (12). Both carbonate and silicate weathering reactions (Eqs. 1 and 2 in Fig. 1) have the potential to consume atmospheric CO₂ dissolved in water (CO₂a(g), but can be limited subglacially due to a lack of CO₂ exchange with the atmosphere (11), and supraglacially due to a lack of comminuted sediments (14). Although the possibility of atmospheric CO₂ consumption by chemical weathering in proglacial freshwaters has been proposed (15, 16), in-depth studies of proglacial freshwater networks have been limited (17–20), with very few in situ measurements of CO₂a(g) despite its importance as an indicator of both freshwater ecosystem function and mineral weathering reactions.

Here we extend the study of chemical weathering beyond the glaciers themselves to the proglacial freshwater drainage network (Fig. 1), using the Lake Hazen watershed (81.8°N, 71.4°W; 7,516 km², 40.9% glacierized) in Quttinirpaaq National Park on Ellesmere Island, Nunavut, Canada, as a model system (SI Appendix, Fig. S1). Ultra-oligotrophic Lake Hazen (544 km², maximum depth = 267 m) is fed by 11 glacial rivers (4.6 to 42 km long) originating from the southeastern outlet glaciers (6 to 1,041 km²) of the Northern Ellesmere Icefield. We sampled 7 glacial rivers across the Lake Hazen watershed to quantify changes in CO₂ fluxes and river chemistry throughout the ablation season (June, July, August [JJAl]). Along 3 of these rivers (Blister, Snow Goose, Gilman), we conducted transects between the glacier termini and their deltas along the Lake Hazen shoreline to assess changes in CO₂ fluxes over space. At 2 of these rivers (Blister, Snow Goose), we also conducted biweekly surveys at their deltas to assess changes in CO₂ fluxes over time. To elucidate the impact of glacial inputs on CO₂ fluxes within Lake Hazen itself, we extended these biweekly surveys to lake

Significance

Glacier melt is one of the most dramatic consequences of climate change in high-latitude and high-altitude environments. As meltwaters move across poorly consolidated landscapes, they transport vast quantities of highly reactive comminuted sediments prone to chemical weathering reactions that may consume atmospheric CO₂. Using a whole-watershed approach in the Canadian High Arctic, combined with additional dissolved CO₂ measurements in glacial rivers in Greenland and the Canadian Rockies, we show that certain glacier-fed freshwater ecosystems are significant and previously unrecognized annual CO₂ sinks due to chemical weathering. As many of the world’s rivers originate from glacial headwaters, we highlight the potential importance of this process for contemporary regional carbon budgets in rapidly changing high-latitude and high-altitude watersheds.


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waters along the northwestern shoreline between the Blister and Snow Goose rivers. Detailed depth profiles of the lake were conducted during the ablation season and under the ice in spring to determine seasonal changes in lake CO$_2$ dynamics, with and without glacial inputs (Fig. 1). We then compared the measured freshwater CO$_2$ fluxes with CO$_2$ fluxes from the adjacent terrestrial environment (polar desert and nonglacial wetlands and ponds) (21, 22) to understand the relative importance of glacial-fed freshwater CO$_2$ cycling in watershed CO$_2$ budgets.

CO$_2$(aq) Consumption in Glacial Inflows to Lake Hazen. In situ concentrations of CO$_2$(aq) across the 7 glacial rivers were below atmospheric equilibrium at all but one of the sites sampled (%CO$_2$ saturation range: 15.2% to 102%, mean ± SD: 70.4 ± 22.7%; SI Appendix, Fig. S2). In contrast, concentrations of dissolved oxygen (O$_2$(aq)) were at or above atmospheric equilibrium at all sites (101 ± 4.10%), showing that turbulent proglacial river waters were well mixed with the atmosphere, and precluding any significant anoxic subglacial contributions. CO$_2$(aq) saturation decreased with increasing distance from the glaciers with a concomitant increase in dissolved inorganic carbon (DIC), cations, and silica (Fig. 2), suggesting the existence of a weathering-dominated system (Box 1, Fig. 1) (23).

If chemical weathering were the predominant mechanism behind the observed CO$_2$ undersaturation, we would expect δ$^{13}$C-DIC to be depleted relative to atmospheric equilibrium because of the kinetic fractionation that occurs after rapid carbonate and silicate weathering. Indeed, δ$^{13}$C-DIC became more depleted at lower CO$_2$(aq). Aside from rapid carbonate and silicate weathering, the only other mechanism that could have resulted in the depletion of δ$^{13}$C-DIC is OC oxidation. However, dissolved organic carbon concentrations in all glacial rivers were extremely low (mean, 0.4 ± 0.2 mg L$^{-1}$; SI Appendix, Table S1), precluding OC oxidation from significantly influencing δ$^{13}$C-DIC, and OC respiration would have resulted in the oversaturation, not undersaturation, of CO$_2$(aq). As such, rapid mineral weathering within the rivers is the most likely process to account for increasing DIC and declining CO$_2$(aq) concentrations over the river lengths, as well as low δ$^{13}$C-DIC values.

Across the proglacial drainage network, geological formations are poorly consolidated after glacial retreat, such that glacial meltwaters can easily erode riverbed sediments and bank deposits (SI Appendix, Fig. S3). This leads to increasing concentrations of suspended mineral sediments capable of weathering in river waters with increasing distance from the glaciers. Indeed, peak glacial river runoff in late July coincided with minimum CO$_2$(aq) and δ$^{13}$C-DIC (Fig. 3).
As weathering reactions consume CO$_2$(aq) in the rivers, CO$_2$(aq) is constantly being replenished from the atmosphere (Fig. 1), but much more slowly than the weathering reactions can consume it (24). As such, in situ CO$_2$(aq) concentrations in proglacial rivers represent the balance between the rate of consumption by chemical weathering and the resupply from the atmosphere. To quantify the capacity for weathering reactions to consume CO$_2$(aq) in the absence of atmospheric exchange at the time of sampling (termed instantaneous weathering potential CO$_2$(aq)), unfiltered river water samples were collected in pre-evacuated serum bottles containing a KCl preservative to prevent biological activity (25). The mean instantaneous weathering potential CO$_2$(aq) saturations were 29.5 ± 35.3%, which is markedly more undersaturated than that measured in situ in the flowing rivers (SI Appendix, Table S1). These potential CO$_2$(aq) concentrations conclusively showed that CO$_2$ consumption was actively occurring in the rivers and was not primarily a result of primary productivity, and that equilibrium with the atmosphere had not been reached at the time of sampling.

Net DIC accumulation along the length of rivers was used as a measure of realized CO$_2$ consumption within the glacial rivers. This approach was adopted in lieu of using CO$_2$(aq) concentrations and calculated gas transfer coefficients (k), the latter of which are extremely variable in rivers, especially braided ones, such as those studied here (26, 27). In the absence of detailed river morphology and water velocities, which were impossible to obtain in our remote High Arctic watershed, the derivation of k from traditional scaling relationships (e.g., refs. 3 and 28) was logistically unfeasible and fraught with uncertainty, necessitating an alternative approach. By relating the increases in cations and silica concentrations to weathering stoichiometry (Eqs. 1 and 2 in Fig. 1), we were able to attribute all (125 ± 13.6%) of the increase in DIC concentration between the glacier termini and river deltas to weathering (Fig. 2 and SI Appendix, Fig. S4), thus further excluding biological processes as important contributors to CO$_2$ dynamics within the glacial rivers.

We estimate that the glacial rivers in the Lake Hazen watershed consumed 1.020 ± 496 Mg C-CO$_2$ y$^{-1}$ through chemical weathering, making the glacial rivers an important and previously overlooked CO$_2$ sink at the watershed scale (Table 1). On an areal basis, the glacial rivers consumed 0.376 ± 1.20 g C-CO$_2$ m$^{-2}$·d$^{-1}$, by far the largest flux (source or sink) in the watershed. This is in stark contrast to rivers globally, which are almost ubiquitously considered net sources of C to the atmosphere (0.66 ± 0.11 g C-CO$_2$ m$^{-2}$·d$^{-1}$) (29). In fact, during the 2016 ablation season (a relatively low melt year), the glacial rivers in the Lake Hazen watershed consumed, on a per square meter basis, about half as much carbon daily (0.085 ± 0.187 g C-CO$_2$ m$^{-2}$·d$^{-1}$) as the Amazon rainforest (0.153 g C-CO$_2$ m$^{-2}$·d$^{-1}$; calculated from refs. 30 and 31). During the 2015 ablation season, when glacial melt was ~3 times that in 2016, CO$_2$ consumption rates in the glacial rivers were, on average, twice that of the Amazon rainforest, with maximum daily rates of up to 40 times higher on a per square meter basis (6.14 g C-CO$_2$ m$^{-2}$·d$^{-1}$).

**Impact of Glacial Inputs on Net CO$_2$ Consumption in Proglacial Lakes.** Similar to other Arctic and alpine glacier-fed lakes, the chemistry of ultra-oligotrophic Lake Hazen is particularly sensitive to geochemical inputs from its catchment (10, 32). Coincident with the start of watershed inputs to the lake in early June, when the lake is still ice-covered, an open-water moat forms around the periphery of Lake Hazen. As the region warms, lake ice melts, and the surface area available for exchange with the atmosphere increases gradually until complete ice off, if it occurs, in late July or early August. Whereas the lake rarely went ice-free before the early 2000s, a late summer ice-free lake is now commonplace (33).

To understand the influence of glacial inputs on CO$_2$ fluxes in nearshore waters of Lake Hazen, we measured in situ CO$_2$(aq) concentrations in nearshore waters and used the wind-speed-derived gas exchange coefficient (k$_{CO2}$) to calculate surface CO$_2$ fluxes (34). After lake ice melt in 2015 (26 July), CO$_2$(aq) concentrations in waters near the shore of Lake Hazen between the inflows of the Blister and Snow Goose rivers ranged between 19.7 and 25.2 μM (mean, 21.8 ± 1.07 μM). The lake surface was a net CO$_2$ sink during the same period, with instantaneous CO$_2$ consumption from lake surface waters averaging 27.1 ± 18.1 μmol m$^{-2}$·h$^{-1}$. Maximum CO$_2$ consumption occurred overnight, likely due to a general increase in wind speed during this time (SI Appendix, Fig. S5). CO$_2$ fluxes in waters near the shore of Lake Hazen were significantly influenced by glacial runoff ($r^2 = 0.21$; F = 9.54; P < 0.001), such that these waters became a progressively greater CO$_2$ sink as glacial melt intensified (SI Appendix, Fig. S6). Chlorophyll a concentrations ranged from below detection to only 0.04 μg L$^{-1}$, suggesting little, if any, primary production in these turbid nearshore waters. As in the glacial rivers, instantaneous weathering potential CO$_2$(aq) concentrations in nearshore waters were significantly lower than in situ CO$_2$(aq) concentrations (paired t test: t = 4.73; P < 0.001), further excluding CO$_2$ consumption by primary producers as the main cause of CO$_2$ undersaturation.
By applying daily ice-free areas on the lake delineated using the MODIS snow cover product (MOD10A1) to the mean daily nearshore CO₂ fluxes during the continuous measurement period (7 July to 2 August 2015), we estimated a mean daily surface CO₂ consumption rate (sum of hourly fluxes, n = 14 d with 24-h records) of 2,570 ± 603 kg CO₂ d⁻¹, translating to an estimated cumulative surface drawdown of 66.7 ± 11.5 Mg CO₂ during the measurement period. However, as glacial inputs to Lake Hazen slowed in August, turbulent mixing in the nearshore region was reduced. The respiration of OC and subsequent production of CO₂ therefore became a relatively more important contributor to net CO₂ fluxes during the shoulder seasons than chemical weathering processes. Thus, when adding the early and late season fluxes measured in 2016 (SI Appendix, Fig. S6) onto the primary open water season, Lake Hazen surface waters were a marginal (<1% of the total annual budget) CO₂ source, emitting 47.7 ± 19.8 Mg C·CO₂ to the atmosphere (Table 1).

At the center of the lake, 4.5 kilometers away from the direct influence of the nearest glacial inflows (SI Appendix, Fig. S1), surface waters were likewise undersaturated in CO₂ during the summer (84.5 ± 3.34%; SI Appendix, Fig. S7). Even at 250 m depth, CO₂ concentrations were 19.4 μM (August 2015) and 24.8 μM (August 2016), corresponding to CO₂ saturations of 72.9% and 93.9%, respectively (O₂ saturation: 101% and 98.2%). CO₂ undersaturation or even equilibrium at depth are highly atypical for large deep lakes, where light penetration and primary productivity are limited to the upper reaches of the water column (35). As dense, sediment-laden glacial river waters flowed into Lake Hazen, they formed turbid underflows, transporting fine particulates and waters with high O₂ and low CO₂ from river deltas to the depths of the lake (SI Appendix, Fig. S7). The magnitude of summer melt was thus the primary control on water column CO₂ concentrations, as the greater glacial melt volume in 2015 was associated with greater CO₂ undersaturation at depth. The observation of CO₂ undersaturation at depth was particularly striking, given that springtime CO₂ undersaturations in bottom waters were up to 476% oversaturated (121 μM). Indeed, summertime oxygenation and CO₂ undersaturation of Lake Hazen bottom waters were historically rare and are believed to be a direct consequence of the intensification of glacial melt in the watershed with a resultant change in lake mixing (36).

To quantify CO₂ consumption by chemical weathering within Lake Hazen as a whole, we calculated annual DIC mass balance budgets for the lake by subtracting DIC inputs from all major water sources (glacial and snow melt waters) from DIC exports out the Ruggles River (36). We then used water column δ¹³C-DIC to attribute net DIC exports from Lake Hazen to respiration or chemical weathering. Lake Hazen was annually a source of DIC (3,150 ± 3,870 Mg C·CO₂ y⁻¹) to the Ruggles River, of which only 12.9% could be attributed to respiration. Given that the remaining DIC must then have originated from chemical weathering, of which half comes from the dissolved CO₂ and the remainder from the comminuted sediments delivered to the lake during the previous summer (Eq. 1 in Fig. 1), we roughly estimated that 43.6% of DIC exports in each year originated from the consumption of CO₂ by carbonate dissolution. Combining these estimates of CO₂ produced by respiration and CO₂ consumed by chemical weathering, we calculated a net CO₂ consumption during low-melt years. We also summed estimates of CO₂ produced by respiration and CO₂ consumed by chemical weathering during high-melt years and low melt years. Due to the dynamic nature of CO₂ production and consumption within lakes, these estimates are approximations of a potentially important process distinct to glacial lakes, which warrants greater research efforts in the future.

Internal CO₂ consumption within Lake Hazen was thus approximately equal to or greater than CO₂ production within the glacial rivers in a given year. Together, these estimates show not only that the influence of the glacial rivers extends far beyond the river channels themselves but also that the magnitude of this net CO₂ uptake due to chemical weathering varies interannually, depending on the volume of meltwaters discharging from the glaciers, such that there would be greater erosion and CO₂ consumption during high-melt years, and less erosion and CO₂ consumption during low-melt years. We also highlight the Ruggles River as a potentially important vector for the delivery of weathering products even further downstream. By summing estimates of net CO₂ consumption in glacial rivers and Lake Hazen itself, we calculate a net aquatic CO₂ uptake within the Lake Hazen watershed of 1,710 ± 1,030 Mg C·CO₂ season⁻¹ (Table 1). Although this aquatic flux is less than that of the more
extensive terrestrial ecosystems that actively produce or consume CO$_2$ throughout the year, the addition of the glacier-fed ecosystems to the budget increased the overall CO$_2$ sink in the watershed by 35% and transformed the summed aquatic components from being a net CO$_2$ source to a net CO$_2$ sink, an important development in our understanding of carbon cycling in these rapidly changing watersheds.

Projected Global Glacial Melt and Downstream Freshwater CO$_2$ Cycling. By 2050, global (non–ice-sheet) glacier volume could decline by between 28% and 44% (37) with coincident near-term changes in glacial river runoff (38). At high latitudes, glacial runoff is expected to increase at least until the middle of the century (38, 39), with yet unknown consequences for the biogeochemistry of receiving aquatic ecosystems (40). Although Lake Hazen is an unusually large body of water for the High Arctic, and thus theoretically more resilient than smaller systems to short-term (seasonal) perturbations (41), we show that the lake is still annually transformed into a CO$_2$ sink by glacial river inputs. Inputs of large volumes of water from projected glacial melt could thus conceivably radically transform the biogeochemistry of smaller, more common freshwater systems.

While the Lake Hazen watershed is underlain by a diverse, carbon-rich geology (42), transient CO$_2$ consumption by weathering processes in glacial meltwaters has also been inferred beneath glaciers in areas dominated by basalt and metamorphic rocks (15, 43), an effect which should extend into the proglacial freshwater network. Although studies directly quantifying the downstream impacts of glacial melt on CO$_2$ are few, CO$_2(aq)$ undersaturation has been observed at other sites in Greenland, Svalbard, Central Europe, and Western Canada (SI Appendix, Table S3). For example, CO$_2(aq)$ concentrations in rivers fed by the Kiatuut Sermiait (Greenland, 61°11.8’N, 45°20.4’W) and Saskatchewan (Alberta, Canada, 52°10.2’N, 117°4.6’W) glaciers, measured using the same technique as in the Lake Hazen watershed, were only 22% and 35% saturated with respect to atmospheric CO$_2$ at locations 2.5 and 5 km downstream of the glaciers, respectively. This strongly suggests that the effects of freshwater CO$_2(aq)$ consumption by sediment-laden glacial meltwaters observed in the Lake Hazen watershed could be relevant across diverse geologies, glacier thermal regimes, and climates.

Understanding the effect of glacier mass loss on carbon cycling in downstream freshwater ecosystems, however, remains challenging. Due to the dynamic relationship between proglacial systems and fluctuating glacier dynamics (44), there exists no published estimate of either the number of proglacial rivers and/or area of proglacial lakes globally, hampering our ability to understand the extent of glacial influence on downstream systems. Our results highlight the importance of glacially fed freshwater systems to the carbon cycle at the watershed scale. We suggest that the effect of glacial melt on CO$_2$ consumption in downstream ecosystems reported here is not limited to the High Arctic (SI Appendix, Table S3) but, rather, is potentially a globally relevant phenomenon meriting greater in-depth study, given future climate change predictions in glacialized regions. On the basis of our results, projected increases in glacial melt imply not only a short- to medium-term increase in water fluxes to downstream ecosystems, but also an increase in the amount and intensity of weathering of highly reactive comminuted sediments being transported downstream, with a concomitant uptake of atmospheric CO$_2$ that has important implications for regional carbon budgets in certain glacialized catchments.

**Methods**

**Study Area.** Lake Hazen, located within Quttinirpaaq National Park on northern Ellesmere Island, Nunavut, Canada, is the world’s most voluminous lake entirely above the Arctic Circle (SI Appendix, Fig. S1). Runoff from the outlet glaciers of the Northern Ellesmere Icefield occurs primarily through supraglacial and ice-channel margins, although subglacial water has been detected for the Henrietta Nesmith Glacier (45). Ice from the Northern Ellesmere Icefield retreated from Lake Hazen ~ 5,000 y ago (46), exposing a diverse geology dominated by the Cambrian Grant Land formation (quartzite, sandstone, schist) to the northwest and the Silurian Daniel River formation (sandstone, carbonate, shale) to the southwest, along the Hazen Plateau (42).

The glacial rivers surveyed in this study drained 2,568 km$^2$ or 84% of the total glacialized watershed area, and extended between 4 and 42 km along defined river valleys before flowing into Lake Hazen. The annual ablation season on northern Ellesmere Island currently extends from early June to late August. Total modeled glacial runoff volumes for the Lake Hazen watershed were 0.98 km$^3$ and 0.29 km$^3$ in 2015 and 2016, respectively (2001 to 2016 mean = 0.47 ± 0.44 km$^3$), with the most important contributions coming from the Henrietta Nesmith, Very, and Gilman glaciers. The Ruggles River (28.8 km) flows year-round, connecting Lake Hazen to Chandler and then Coneybeare fjords on the northeastern coast of Ellesmere Island. The Lake Hazen watershed is located within the continuous permafrost zone, and although active layer thaw occurs, it is hydrologically insignificant. Total precipitation for the nonglacierized area of the Lake Hazen watershed is ~95 mm (47).

Snowmelt on the landscape and lake ice surface occurs in late May/early June, followed by a short decrease in runoff before melt from the glacialized area begins in late June. Rainfall during the summer (JJA) ablation season has been previously recorded as only ~34 mm (2008 to 2012 mean) (21). During summer, snowfall ceases when meltwater flows falling outside the receiving freshwater continuum. Because of the period of this study, the ablation seasons extended from ~2 June to 17 August (2015), and 5 June to 28 August (2016). No meltwaters are discharged from the glaciers outside of this period. Mean annual air temperatures for 2015 and 2016 at Alert (82.5°N, 62.3°W) and Eureka (80.0°N, 85.9°W), the closest permanent weather stations, were ~14.8 ± 1.3 °C and ~17.5 ± 0.8 °C, respectively (Environment and Climate Change Canada).

Water samples were collected during summers 2015 (6 July to 2 August) and 2016 (6 July to 8 August), focusing on Lake Hazen itself in 2015 and on the glacial rivers in 2016. In so doing, we surveyed the entirety of the arctic freshwater continuum from the glacier termini through to the receiving freshwater ecosystems (river and lake). Details on sample collection and analysis can be found in the SI Appendix.

**Glacial Rivers.** CO$_2$ consumption calculations. Proglacial CO$_2(aq)$ fluxes were calculated for the glacial rivers, using the changes in DIC concentrations along the transects of the Blister, Snow Goose, and Gilman rivers (n = 5) and relating these changes to weathering stoichiometry (11). Every 1 mol increase in Ca$^{2+}$ and Mg$^{2+}$ between the glacier terminus and the river delta consumes 1 mol CO$_2(aq)$ via carbonate dissolution (Eq. 1 in Fig. 1), with Ca$^{2+}$ concentrations corrected for the increase in SO$_4^{2−}$ over the same distance. Further, a 1 mol increase in SO$_4^{2−}$ consumes 2 mol CO$_2(aq)$ via sulfate dissolution, although this CO$_2$ enhancement assumes stoichiometric dissolution, which does not always occur (20), silicate weathering conservatively accounted for only 1.50 ± 0.65% of the DIC increase across all transects. Using this approach, we accounted for 125 ± 13.6% of the DIC increase over the length of the glacial rivers (SI Appendix, Fig. S4), validating our use of the change in DIC concentration along the river lengths as a metric of CO$_2$ consumption.

To estimate DIC concentrations at the glacier termini on rivers and days for which transects were not completed, we applied a mean DIC concentration corrected for the increase in CO$_2(aq)$ consumption at high pH (49, 50):

$$\Delta [\text{DIC}] = \Delta [\text{CO}_2(aq)] - \frac{\text{DIC}_{\text{end}} - \text{DIC}_{\text{start}}}{\text{DIC}_{\text{end}} - \text{DIC}_{\text{start}}} \times \text{DIC}_{\text{end}}$$

where $\Delta [\text{DIC}]$ is the change in DIC concentration along the river length, $\text{DIC}_{\text{end}}$ and $\text{DIC}_{\text{start}}$ are DIC concentrations at the glacier terminus and the river delta at Lake Hazen, respectively, assuming no additional water sources to the rivers downstream of the glaciers, we subtracted the daily modeled DIC load at the glacier from the DIC load at the lake (SI Appendix, Table S4). We attributed this change in DIC load to dissolution reactions (CO$_2(aq)$ consumption and consequent HCO$_3^−$/DIC production) in the rivers. The difference was then halved to account for the fact that 1 product concentration at the glacier terminus:

$$\text{Flux} (\mu\text{mol} \text{m}^{-2} \text{h}^{-1}) = k_{\text{CO2}} \Delta [\text{CO}_2(aq)],$$

where $k_{\text{CO2}}$ is the gas exchange coefficient calculated from mean hourly wind speed (in m s$^{-1}$), $\Delta [\text{CO}_2(aq)]$ is the difference between the CO$_2$ concentration measured in situ and the CO$_2$ concentration that would occur if the waters were at atmospheric equilibrium, calculated using Henry’s Law, and in situ temperature
and barometric pressure. To calculate enhanced fluxes when there was no associated pH measurement, we applied a median enhancement factor of 18% (n = 350) to the under-ice DIC fluxes. The conservative budget based on the mean (25%) and range of enhancement factors observed (2% to 97%). Net ablation season CO₂ exchange from the Lake Hazen surface in both 2015 and 2016 was estimated from the measured daily flux multiplied by the daily ice-free area, extracted from the MODIS snow cover product (MOD10A1) (33). For days when net daily fluxes were not measured, we used the mean of the previously and subsequently measured daily fluxes. To extrapolate the data outside of the measurement period, we applied the first (2 July-August) measured fluxes from 2016 were applied to the periods before or after measurement, respectively. Values for 2016 were also applied to the shoulder seasons in 2015, when a shorter field campaign was undertaken.

Lake Hazen Water Column (Internal).

CO₂ consumption within Lake Hazen. CO₂ consumption within the Lake Hazen water column was calculated by constructing a DIC mass balance budget for Lake Hazen in both 2015 and 2016. Briefly, hydrological inputs of DIC to the lake were the sum of glacial river (described here, using the surface mass balance approach and LOADES log-linear models) and snow meltwater inputs (described in detail in ref. 36), while the sole hydrological output of DIC from the lake was via the Ruggles River. Ruggles River discharge was estimated as the sum of all hydrological inputs to the lake. The difference between DIC inputs and outputs thus reflects processes occurring within the water column itself, where DIC is produced by chemical weathering and heterotrophic respiration, or consumed by primary productivity, which is negligible in ultralimnol. J. Geophys. Res. Biogeosci. 121, 864–878 (2016).


