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Supplement of

Sources, cycling and export of nitrogen on the Greenland Ice Sheet

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Supplementary Information

1 Moulin discharge measurements and chemical time series

Water flow into the sampling moulin was monitored continuously by measuring water level (stage) and then converting stage to flow rate via an empirically-derived stage-discharge curve. Details are provided in the following sections.

1.1 Stage measurements

Stage was measured using a custom-built water pressure sensor comprising a Honeywell 26PCBFA6D differential pressure sensor, instrumentation amplifier and associated electronics housed in aluminium tubing filled with potting resin. Differential voltage output from the sensor was recorded at 60 s intervals on a Campbell Scientific CR10X data logger. Pressure sensors were secured with several steel weights within crevasse traces which cross-cut supraglacial streams which tend to remain incised into the channel base. The assembly was secured to the bank using ropes. A compromise was necessary between siting the sensor centrally in the channel, from where the increased drag on cables and ropes made it more likely to become dislodged, and siting it closer to the edge where the sensor placement was more secure but the water level sometimes dropped below the sensor. When re-siting was necessary, resulting step-changes in the stage record were used to correct for the difference in water depth between the old and new sites.

1.2 Discharge measurements

Salt dilution gauging was used to obtain point measurements of discharge. This method is particularly well suited to meltwater streams, because the background salt concentration is very low (EC typically $2 \mu\text{S cm}^{-1}$). For each measurement a known quantity of domestic salt (typically 50-200 g) was completely dissolved in a known volume of water in a bucket (typically 2 – 5 L). The bucket contents were then ejected close to the centre of the stream ~200 m up-stream of an EC sensor. The EC sensor comprised five parallel copper electrodes housed in a plastic tube. The sensor was wired in series with a fixed resistor ($100 \text{ k}\Omega \pm 0.1\%$), and a Campbell Scientific CR10X data logger was used to measure the resistance across the sensor electrodes at 1 s intervals. To calibrate the sensor, successive dilutions of the injected salt solutions were carried out to establish a relationship between change in sensor resistance (R_s) and added salt concentration C (Suppl. Figure 1), yielding time series of added salt concentration from which the stream discharges were calculated (Suppl. Figure 2). The calibration curve for C (Suppl. Figure 1) was calculated by second-order polynomial

regression of $C^{1/2}$ against $1/R_S$, specifically $C^{1/2} = a(1/R_S)^2 + b(1/R_S)$ where a and b are constants. This particular curve satisfies two key requirements: (1) the curve passes through the origin (such that zero change in $1/R_S$ corresponds to zero added salt; and (2) $C \geq 0$ for the range of $1/R_S$ values relevant to the dilution gauging. By setting $y = C^{1/2}$ and $x = 1/R_S$, coefficients a and b are determined using least-squares regression of the function $y = ax^2 + bx$. If E is the sum of squared residuals, we can use the standard approach of finding where $\partial E/\partial a = \partial E/\partial b = 0$, with solution:

$$a = \frac{\sum_i x_i^2 y_i \sum_i x_i^2 - \sum_i x_i y_i \sum_i x_i^3}{\left(\sum_i x_i^4 \sum_i x_i^2 - \left(\sum_i x_i^3 \right)^2 \right)}$$

$$b = \frac{\sum_i x_i^2 y_i - a \sum_i x_i^4}{\sum_i x_i^3}$$

Supp. Eq. (1)

The coefficient of determination is $r^2 = 1 - E/\sigma_y^2$, where σ_y^2 is the variance of y . Applying these calculations to the data plotted in Suppl. Figure 1:

$$C = [-1.57 \times 10^{-3}(1/R_S)^2 + 0.104(1/R_S)]^2$$

Supp. Eq. (2)

with $r^2 = 0.97$.

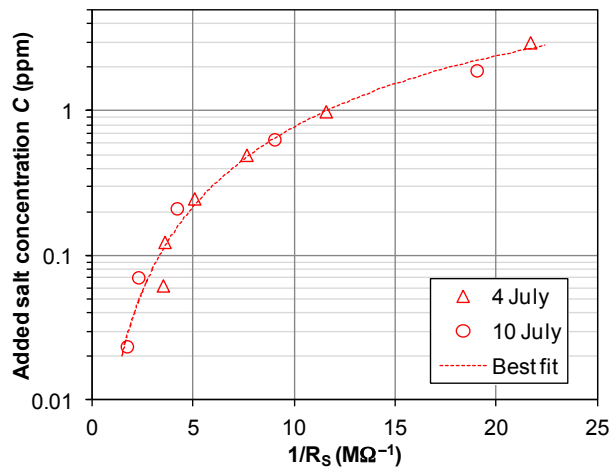
If the added salt concentration (in ppm) recorded in the river over a time period T is $C(t)$, and M kg of salt were added, then discharge Q ($m^3 s^{-1}$) during the course of the dilution experiment is

$$Q = \frac{M}{\rho_w \int_T 10^{-6} C(t) dt}$$

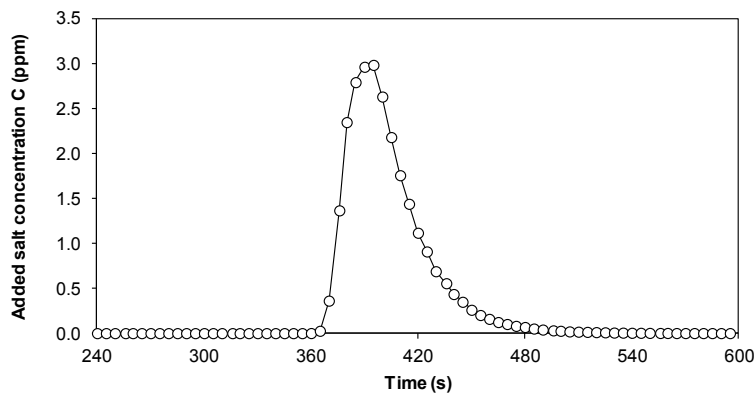
Supp. Eq. (3)

where ρ_w is the density of the river water (assumed to be 1000 kg m^{-3}). Since the concentration data were obtained at discrete time points the integral was calculated using the trapezium rule.

Supplementary Figure 1 Calibration curve to convert measured EC sensor resistance R_S to added salt concentration C .



Supplementary Figure 2 Example salt trace on 4 July, 17:00.



1.3 Stage-discharge relationship

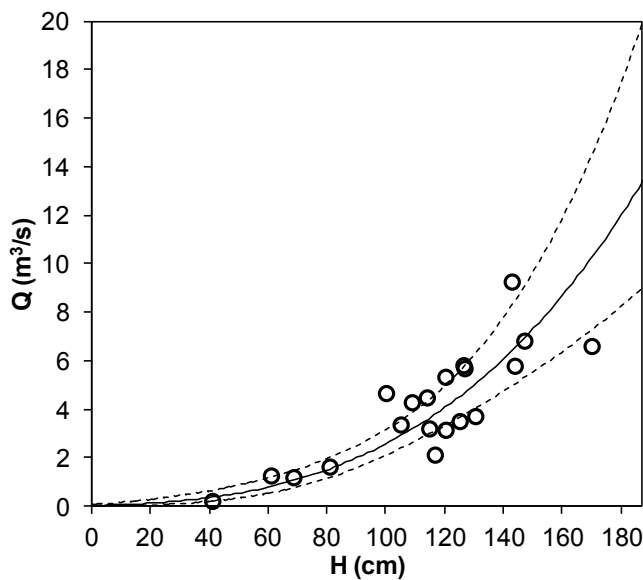
To convert stream stage measurements to discharge, a rating curve was established using measurements of discharge obtained from a total of 20 salt dilutions. Following common practice the rating curve had the form:

$$Q = A(H - H_0)^p. \quad \text{Supp. Eq. (4)}$$

The parameters A , H_0 and p are assumed to be constants, which may not be the case for an ice-walled channel if the channel geometry changes with time; nevertheless, we adopted this assumption noting that resulting errors (as well as random errors arising from the salt dilution method) can be estimated using residuals from the rating curve. The parameter H_0 is an offset introduced because the sensor was generally not located at the lowest point in the channel cross-section, i.e. the sensor read zero when there was non-zero flow. H_0 is therefore the

hypothetical stage reading when $Q = 0$, and should be negative. To determine the values of the three parameters, A and p were calculated using least-squares regression (of $\ln Q$ on $\ln H$) for a range of negative H_0 values from -50 to -10 cm. Varying H_0 had very little effect on r^2 , which varied from 0.84 to 0.85 over the above range of H_0 . For most river stages the rating curve shows little sensitivity to the choice of H_0 , for example with $H_0 = -50$ and -10 cm, the respective mean discharges were 3.5 and $3.4 \text{ m}^3 \text{ s}^{-1}$; respective maximum discharges were 12.6 and $11.8 \text{ m}^3 \text{ s}^{-1}$. An intermediate value of $H_0 = -30$ cm was therefore adopted. The rating curve is shown in Suppl. Figure 3.

Supplementary Figure 3 Rating curve established using salt dilution gauging. The solid line is the best fit with $H_0 = -30$ cm, and the dashed lines are 95% confidence intervals.

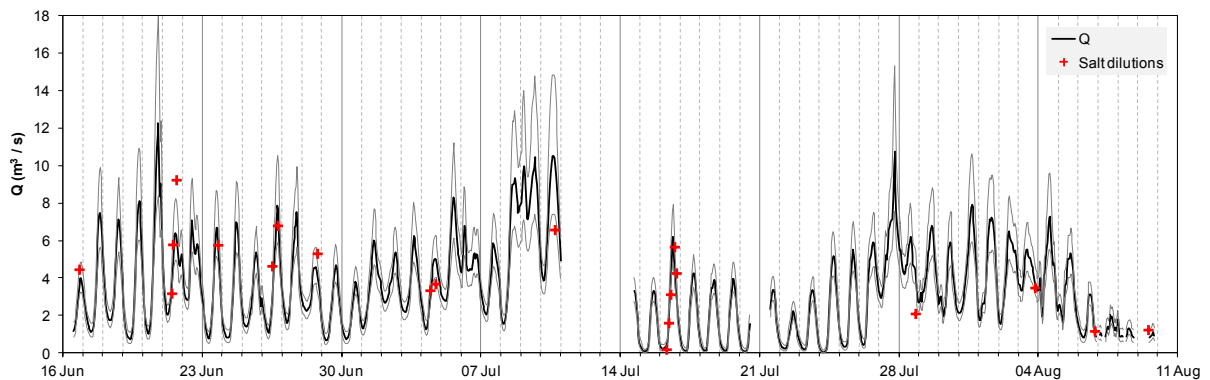


Confidence intervals for the discharge time series were calculated using the rating curve regression statistics. There are n pairs of stage and discharge measurements (H_i, Q_i) ; $i = 1 \dots n$. Let $X = \ln(H - H_0)$ and $Y = \ln Q_i$. X has variance s_X^2 and mean \bar{X} . Linear regression of Y on X yields intercept $\ln A$ and slope p . Residuals $\varepsilon_i = Y_i - (\ln A + pX_i)$. The confidence interval $[Y_-, Y_+]$ for Y at point (X, Y) is:

$$[Y_-, Y_+] = \left[\ln A + pX \pm t_c \sqrt{\left(\frac{1}{n-2} \sum \varepsilon_i^2 \right) \left(\frac{1}{n} + \frac{(X - \bar{X})^2}{(n-1)s_X^2} \right)} \right] \quad \text{Supp. Eq. (5)}$$

where t_c is the $(p/2)$ -th quantile of the t distribution with $n-2$ degrees of freedom and p is the probability level. The corresponding confidence interval for Q is therefore $[Q_-, Q_+] = [\exp(Y_-), \exp(Y_+)]$. The time series of stream discharge is shown with 95% confidence intervals in Suppl. Figure 4. The long gap in mid-July was caused by problems with anchoring the pressure sensor after it became dislodged in the sustained high flow of the previous 3 days. There is greater uncertainty in the peak flow rates because the corresponding stages lie outside the range of the rating curve.

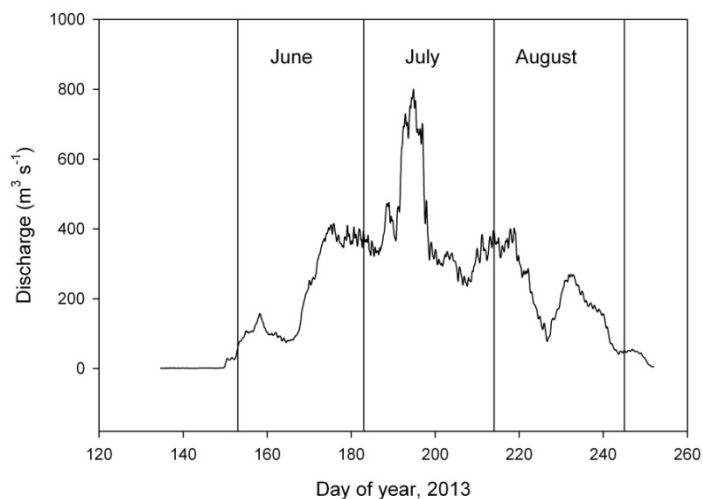
Supplementary Figure 4 Discharge record (black line) with 95% confidence intervals (grey lines) and individual discharge measurements (red crosses).



2. Seasonal water fluxes

The 2012 melt season was the highest melt year on record in Greenland¹⁵. The runoff time series at LG in this year is presented in Supplementary Figure 5.

Supplementary Figure 5 Time series of bulk meltwater discharge measured at the margin of Leverett Glacier in summer 2012.



2 Moulin nutrient concentrations and fluxes

Supplementary Figure 6 Time series of nitrogen species concentrations in moulin waters compared with those in runoff for a) TDN, b) DON, c) dissolved nitrate, d) dissolved ammonium and e) time series of the instantaneous fluxes of N species in moulin waters, when plotted alongside moulin water fluxes (Q), measured at the entry point to the moulin (see Suppl. Info. 1)

