Biogeosciences

Supplement of

Proglacial methane emissions driven by meltwater and groundwater flushing in a high-Arctic glacial catchment

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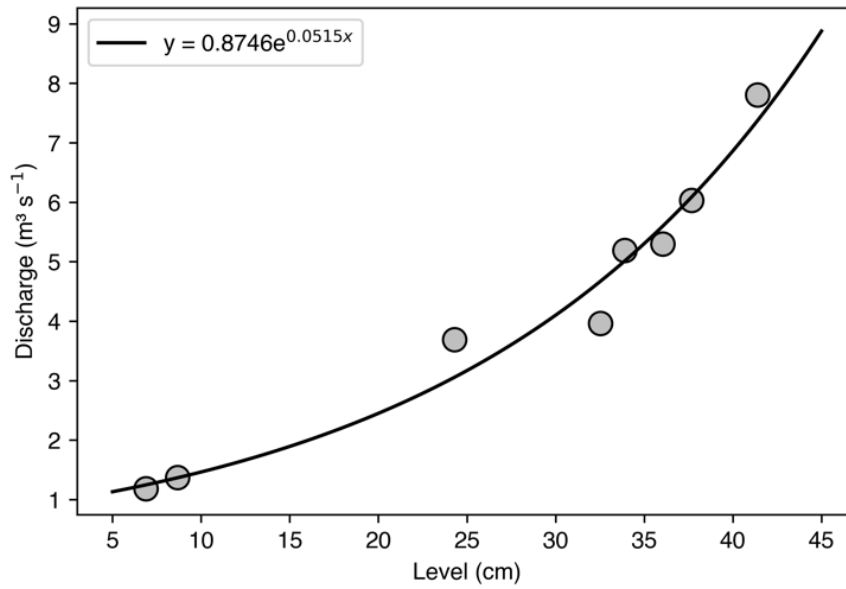
Supplementary Figures and Tables

Figure S.1. *Calibration of hourly stage measurements (cm) with discharge (m^3 s^{-1}) using 8 discharge measurements throughout the summer, $R^2 = 0.97$.*

Figure S.2. (a) *GW1 spring outflow, with outlet stream flowing towards the top left corner of the picture,* ***(b)*** *GW2 pool—pool formed over the inflow of the spring with outlet stream marked with red arrow,* ***(c)*** *The bubble trap used to make ebullition measurements, and* ***(d)*** *bubbles resulting from ebullition trapped beneath a thin layer of ice formed on the surface of the GW2 pool during a period with below-freezing temperatures at the end of the summer.*
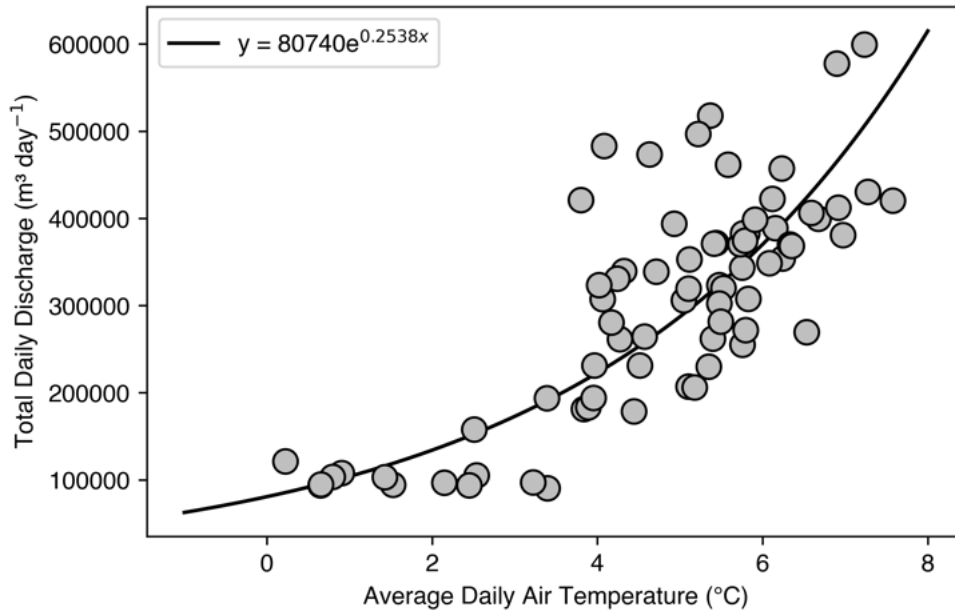
Figure S.3. *Relationship between total daily discharge from the Vallåkrabreen melt river and the average daily air temperature measured at Sveagruva (seklima.met.no), $R^2 = 0.59$.*

Sediment chamber measurements

The diffusive flux of methane from sediments within the proglacial forefield was measured using a chamber box in six locations throughout the glacier floodplain. A small electrical fan was fixed inside the box to maintain airflow within the chamber. Samples of the air within the box were taken four times for each deployment, starting immediately after placing the chamber down and finishing after 45 minutes. Air samples of 5 mL were injected into pre-evacuated 3 mL Exetainer vials. Methane concentration measurements of the chamber air samples were made at the University of Tromsø with a gas chromatograph fitted with a flame ionization detector (GC-FID; ThermoScientific, Waltham, MA USA).
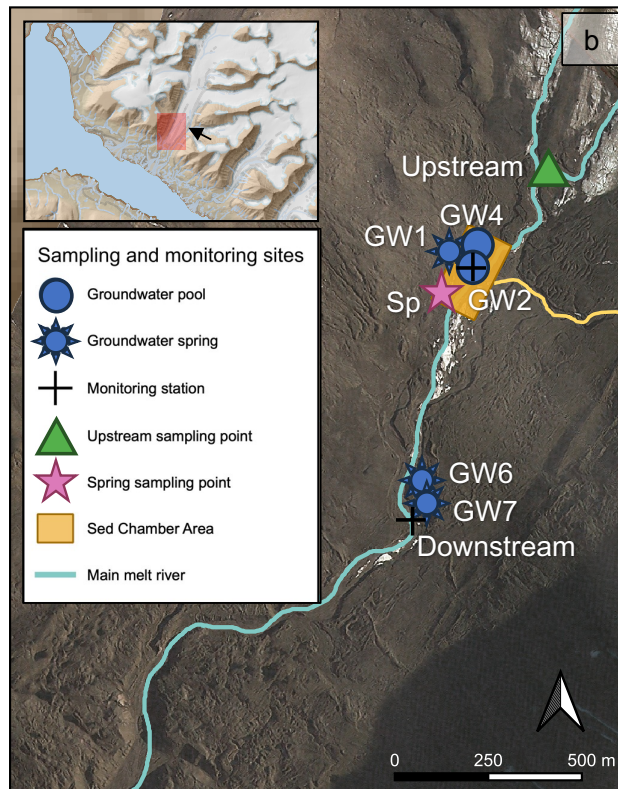
Figure S.4. *Map of the Vallåkrabreen forefield indicating the area in which the sediment chambers were deployed (in orange).*
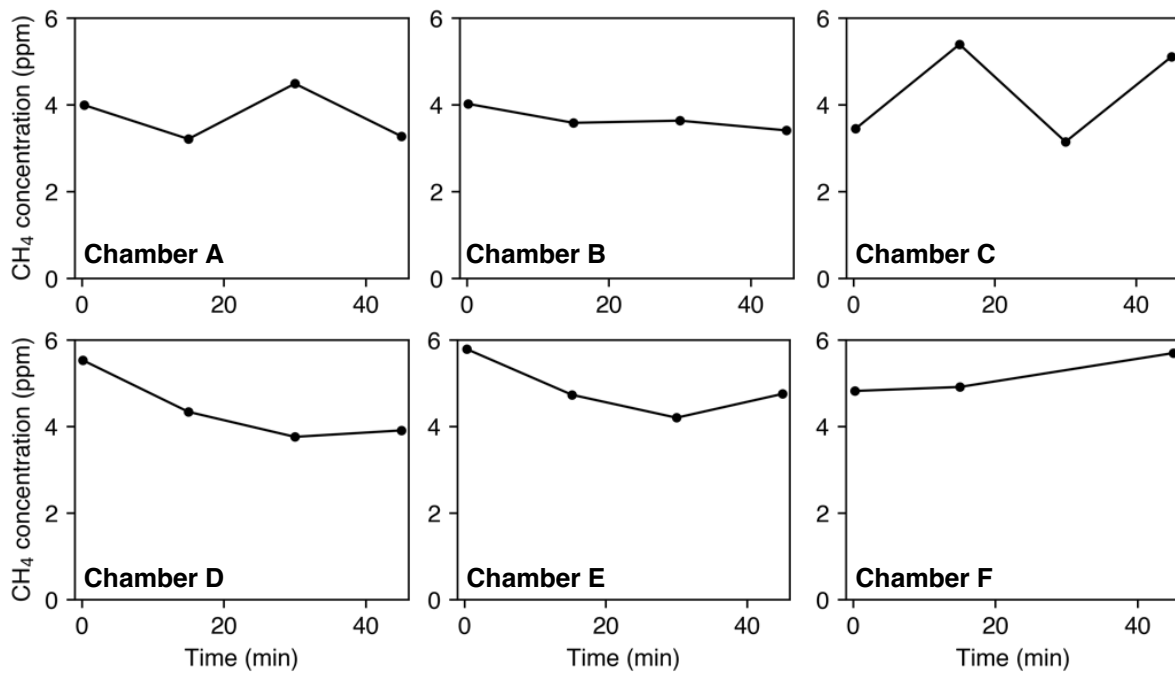

Figure S.5. *Sediment chamber measurements taken on 07 September 2021.*

Ethane and propane measurements of the melt river

The ethane and propane concentrations of two melt river samples from 2023 were measured, and the corresponding wetness values ($C_1/(C_2+C_3)$) were calculated. Samples were prepared for analysis by replacing 4.6 ml of sample water in the 22 mL crimped headspace vials with laboratory grade Helium (5.9) and then left to equilibrate at the laboratory temperature of 20°C for at least 2 hours.

The total headspace pressure was measured using the evacuable sample injection system of the gas chromatography system (Trace 1310 GC, Thermo Fischer Scientific, USA) which was equipped with three heated sample loops and a valve system with column switching. One mL of sample was injected into evacuated three parallel sample loops with a known dead volume. The total pressure in the system before injecting on the columns was measured using a Keller® pressure transducer (PAA-25, range 0 to 200 kPa, 0.4 kPa accuracy) and the total headspace pressure in the gas phase of the vial was subsequently calculated from the sample loop pressures. Total headspace pressures after equilibration were ranging between 100kPa and 107.5kPa.

The individual gas components were quantified in parallel on three channels. On channel 1, pre-separation of hydrocarbons (methane through hexane) from the 500 μL sample loop was performed on a non-polar polysiloxane polymer column (Restek MX-1, 15 m, 0.28 mm ID, film thickness 3 μm) which allows to back-flush higher molecular weight components $>C_6$. Main separation was carried out on a 50 m Al_2O_3 capillary column (0.32 mm ID, film thickness 5 μm), eluting components were quantified on a Flame Ionization Detector (FID) with helium (He) as carrier gas. On channel 2, the sample was injected via a 500 μl sample loop. CO_2 was separated from other components by a pre-column (30 m Hayesep Q, 0.53 mm ID, film thickness 20 μm) and directly quantified after by-passing the main analytical column on the thermal conductivity detector (TCD). All other components (Ne, H_2, Ar, O_2, N_2, CH_4, and CO) were chromatographically separated on the main analytical column (80 m Molsieve 5 Å, 0.53 mm ID, film thickness 50 μm). Carrier gas on this channel was He. For better sensitivity for helium and hydrogen, these compounds were analysed on an additional channel with Argon as carrier gas. The sample loop used had a volume of 125 μl. CO_2 and higher molecular weight carbon-components were retained and back-flushed on a packed pre-column (2 m Hayesep Q 1/16" OD, mesh 100/120, 1 mm ID). Separation of He, Ne, H_2, O_2, and N_2 was achieved on a

5 Å packed molecular sieve column (3 m, mesh 80/100, 1 mm ID) and the components subsequently quantified on the TCD. All columns above were operated non-isothermally starting at 35 °C (hold 7.5 minutes) followed by subsequent heating with 16°C/min to 180 °C (holding 1 minute).

The concentrations of methane, ethane and propane were calculated using the partial pressure, derived from fractional concentration and total headspace pressure, temperature of the sample, volume of headspace gas and remaining water applying the individual Henry's Law constants as listed by Sander (2015). The corresponding wetness values ($C_1/(C_2+C_3)$) were then calculated.

Table S.1. Wetness values, calculated as $C_1/(C_2+C_3)$, of the Vallåkrabreen melt river.

Sample	Date	Wetness
Vallåkrabreen Upstream	19-Jul-23	91
Vallåkrabreen Upstream	31-Jul-23	62

Supplementary References

Sander, R.: Compilation of Henry's law constants (version 4.0) for water as solvent, Atmospheric Chemistry and Physics, 15, 4399–4981, https://doi.org/10.5194/acp-15-4399-2015, 2015.