



1 **Downstream export dominates the fate of groundwater-derived CO₂ in**
2 **a boreal stream**

3 Carolina Olid^{1*}, Demian Hauptmann², Jan Karlsson², Marcus Klaus³

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5 ¹UB-Geomodels Research Institute, Department of Earth and Ocean Dynamics, University of
6 Barcelona, Barcelona, Spain

7 ²Department of Ecology, Environment and Geoscience, Umeå University, Umeå, Sweden

8 ³Department of Forest Ecology and Management, Swedish University of Agricultural Sciences,
9 Umeå, Sweden

10

11 *Correspondence to:* Carolina Olid (carolina.olid@ub.edu)

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15 **Abstract**

16 Groundwater inflow is increasingly recognized as a major source of carbon dioxide (CO₂) to
17 streams. Yet, its fate - whether it is emitted to the atmosphere or exported downstream - remains
18 poorly characterized, partly due to the challenges of quantifying groundwater inflow rates at high
19 spatial (meter) and temporal (days) resolutions. In this study, we assessed the fate of groundwater-
20 derived CO₂ in a 400 m boreal headwater stream reach by combining fine-scale measurements of
21 groundwater inputs, emissions and downstream export of CO₂. Spatial patterns in groundwater-
22 derived CO₂ inputs were primarily driven by the magnitude of groundwater inflows, which were
23 controlled by catchment characteristics, such as stream slope and localized aquifer properties.
24 Temporally, peaks in groundwater CO₂ inputs during snowmelt were primarily driven by increased
25 groundwater discharge rather than elevated CO₂ concentrations in the groundwater, whereas peaks
26 during summer and early autumn were associated with rainfall events and higher CO₂
27 concentrations in groundwater, likely resulting from enhanced soil respiration. Overall,
28 groundwater CO₂ inputs exceeded CO₂ emissions by up to fourfold, with 40-60% of terrestrial CO₂
29 transported downstream. This indicates that a substantial portion bypasses immediate atmospheric
30 emission and may contribute to CO₂ emission further along the stream network or be cycled
31 through in-stream processes downstream. Our results demonstrate how and to what extent
32 groundwater inflows contribute to the variability of CO₂ fluxes from headwater streams. These
33 findings highlight the importance of integrative assessments of CO₂ fluxes (i.e. groundwater
34 inputs, emissions, and downstream export), which consider both in-stream processes and
35 catchment-scale dynamics. This is particularly important in the context of climate-driven changes
36 in hydrology and terrestrial carbon cycling.

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39 1 Introduction

40 Inland waters play a critical role in the emission of carbon dioxide (CO₂) into the atmosphere
41 (Raymond et al., 2013). Global assessments of riverine CO₂ emissions suggest that rivers and
42 streams almost balance out the terrestrial ecosystems' carbon (C) uptake and are of similar
43 magnitude as the net ocean CO₂ uptake from the atmosphere (Drake et al., 2018). Among riverine
44 systems, headwater streams (i.e., first to third-order streams using the Strahler number) are
45 particularly important because they contribute to more than 70% of global riverine CO₂ emission
46 while representing only 17% of river surface area (Li et al., 2021). Yet, despite progress in
47 understanding the role of headwater streams in the global C cycle, uncertainties remain regarding
48 the underlying mechanisms regulating these fluxes.

49 In the boreal biome, which holds approximately one-third of the Earth's terrestrial C stocks
50 (Bradshaw & Warkentin, 2015), headwater streams are both numerous and characterized by
51 elevated CO₂ concentrations (Rasilo et al., 2017; Wallin et al., 2018). The frequent CO₂
52 supersaturation observed in these systems has been linked to *in-situ* mineralization of terrestrial
53 organic C (OC), alongside abiotic processes such as weathering and photooxidation (e.g. Rasilo et
54 al., 2017). However, recent attention has increasingly focused on lateral inputs from groundwater,
55 particularly in small streams that are strongly connected to the surrounding soils and groundwater
56 (Duvert et al., 2018; Hotchkiss et al., 2015; Lupon et al., 2019). While much of the CO₂ derived
57 from groundwater is likely to be emitted to the atmosphere when it enters the stream, some fraction
58 may be transported downstream, where it can be emitted or processed via in-stream
59 biogeochemical pathways. While the relative contributions of groundwater and in-stream sources
60 remain unclear, the dual role of groundwater as both a driver of local CO₂ emission and a
61 contributor to downstream C fluxes may have important implications for our understanding of C
62 dynamics across the land-to-ocean continuum.

63 Catchment characteristics such as hydraulic gradient, vegetation cover, and soil moisture
64 modulate the magnitude and location of groundwater discharge, while external factors like
65 precipitation also influence discharge patterns (Leith et al., 2015; Olid et al., 2022), which in turn
66 introduces spatial and temporal variability in both groundwater CO₂ inputs and their subsequent
67 fate (i.e. emission vs. export). Heterogeneity in groundwater flow paths may explain the patchiness
68 observed in CO₂ emissions, as well as variability in the fraction of CO₂ transported downstream
69 along stream reaches (Hotchkiss et al., 2015a; Ledesma et al., 2018; Lupon et al., 2019). Although
70 some studies support the significance of terrestrial CO₂ inputs via groundwater to stream CO₂
71 dynamics, most evidence remains indirect. Only a few studies have quantified the magnitude of
72 groundwater CO₂ inputs to streams (Avery et al., 2018; Biehler et al., 2023; Call et al., 2018;
73 Hotchkiss et al., 2015), and even fewer have examined their spatial and temporal variability (Lupon



et al., 2019), limiting our ability to understand the patterns and processes that control CO₂ dynamics in stream networks.

Various methods have been used to estimate groundwater inflow rates to streams, including temperature profiling (Briggs et al., 2012; Westhoff et al., 2011), electrical conductivity (Baxter et al., 2003), stream gauging (Cook, 2015; Schmadel et al., 2010), seepage meters (Boyle, 1994, Libelo & MacIntyre, 1994), and mass balance approaches (Rasilo et al., 2017; Rosenberry, 2008). However, these techniques often rely on simplifying assumptions and lack the resolution needed to capture the spatial and temporal variability of groundwater contributions. In contrast, dynamic assessments over days to weeks are possible through the natural radionuclide radon (²²²Rn), which has gained recognition as a powerful tracer for quantifying groundwater-surface water exchange due to its high enrichment in groundwater, conservative behaviour, and short half-life ($T_{1/2} = 3.8$ days) (Adyasari et al., 2023; Burnett et al., 2001). These properties make ²²²Rn particularly well-suited for detecting fine-scale variability in groundwater inflows and their potential role in stream CO₂ dynamics. Nonetheless, studies explicitly linking ²²²Rn-based groundwater inflow estimates to CO₂ emissions or downstream C export remain scarce and are often limited to short-term, low-flow conditions (Avery et al., 2018; Biehler et al., 2023; Call et al., 2018).

In this study, we investigated the role of groundwater inflow in regulating CO₂ emissions and downstream export in a boreal headwater stream. Using ²²²Rn as a tracer, we assessed spatial and temporal patterns of groundwater inflow rates and associated CO₂ inputs during the ice-free period (from April to September). We hypothesized that groundwater inflow shapes CO₂ concentration patterns along the stream by acting as a direct source of CO₂. We expect a large fraction of terrestrial CO₂ delivered via groundwater to be rapidly emitted to the atmosphere upon entering the stream, but also a significant portion to be transported downstream. We further hypothesize that the influence of groundwater inflow on both stream CO₂ emissions and downstream export varies across space and time, likely driven by differences in topography and hydrological conditions.

2 Material and Methods

2.1 Study area

Our study focuses on Torrkälsbäcken, a headwater stream in northern Sweden (Fig. 1). The study region has a cold, humid boreal climate with a prolonged snow cover, typically lasting 167 days during the winter (1981-2015; Hjalmar Laudon & Ottosson Löfvenius, 2016). The average annual temperature recorded at the nearby Svartberget research station is 2.1 °C (1986-2015), with a minimum of -8.6 °C in January and a maximum of 14.6 °C in July. The average annual precipitation is 619 mm, of which about 30% falls as snow (Hjalmar Laudon et al., 2021).

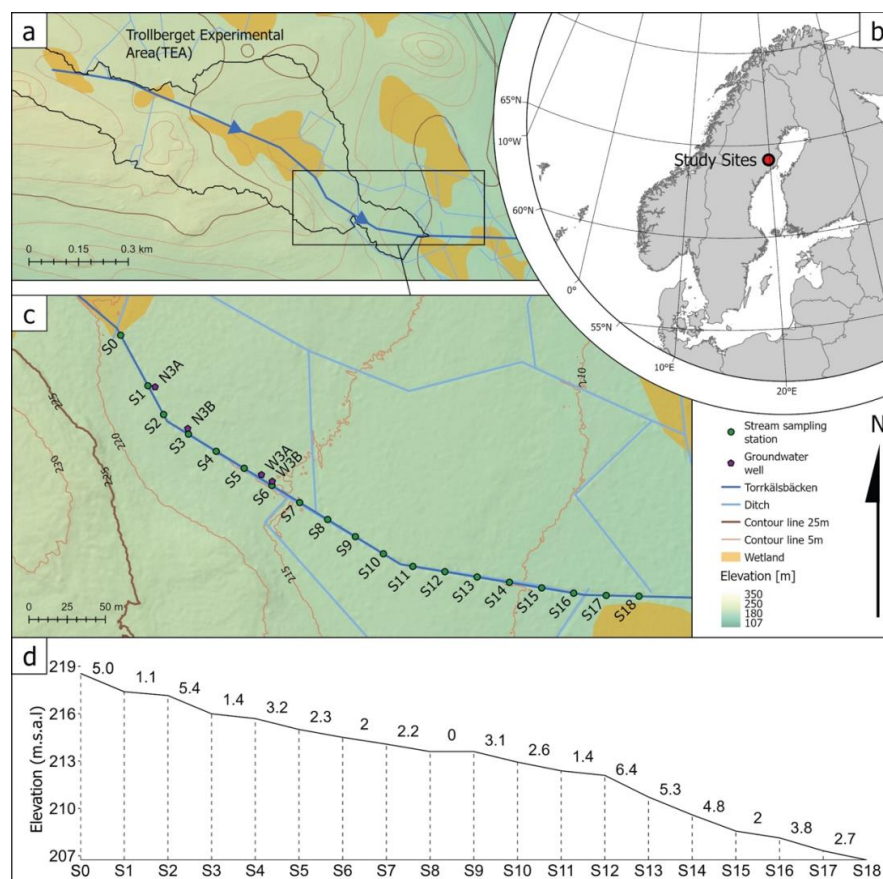


Figure 1: (a) Location of the Trollberget Experimental Area (TEA), (b) a close-up of the study reach within TEA, (c) relative location within northern Europe and d) Elevation profile (in m) and slope (%) along the sampling stations of the stream (Hauptmann et al., in revision). Locations of the outlet of an open mire (S0) and sampling stations (S1-S18) are shown in green circles. Locations of groundwater wells (G1, G3, G5, and G6) are shown in purple stars. Map created using *Terrangkartan* and 0.5 Digital Elevation Model (DEM). Data provided by Lantmäteriet (© Lantmäteriet).

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110 Forest growing on podzol developed in glacial till covers 87% of the Torrkällsbäcken
 111 catchment area and consists mainly of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea*
 112 *abies* (L.) H. Karst.), also featuring birch (*Betula ssp.*), and scattered occurrences of alder (*Alnus*
 113 *incana* (L.) Moench), aspen (*Populus tremula* L.), and willow (*Salix ssp.*) in the riparian areas.
 114 The remaining 13% of the catchment is covered equally by open mire and forest on mire.
 115 Torrkällsbäcken was ditch-trenched and straightened in the 1920s or 1930s to increase drainage



116 and hence timber production (Hasselquist et al., 2017; Norstedt & Laudon, 2019). This work
117 introduced ditches as tributaries, affecting the hydrology of the stream (Fig. 1b). Since then, the
118 stream has developed a riffle structure interspersed with occasional runs and step-pool systems.
119 Pools and runs can reach wetted widths of up to 2 m, while riffle sections typically have an average
120 width of 30 cm. The stream's hydrology is strongly influenced by snowmelt, resulting in peak water
121 flows during spring flood, typically at the end of April (Laudon et al., 2013). Baseflow discharge
122 varies between 0.5 and 2.0 L s⁻¹ and is typical for the summer period (Hauptmann et al., in
123 revision). A dense moss layer (*Polytrichum* spp. Hedw., *Sphagnum* spp. L.) predominates the
124 ground vegetation alongside the stream within the channel, including areas that are periodically
125 inundated, while dwarf shrubs (*Vaccinium myrtillus* L., *Vaccinium vitis-idaea* L.) dominate along
126 the hillslope.

127 Our study quantified groundwater inflow rates and their influence on CO₂ emissions and
128 export along a 400 m stretch of Torrkällsbäcken stream, beginning just downstream of a 2-ha open
129 mire (Fig. 1b, S0) and continuing through forested podzol soil areas (Kuglerová et al., 2013;
130 Laudon et al., 2020). The study reach comprises a transect of 18 sampling stations (S1–S18), where
131 stations were distributed at 20 m intervals at elevations ranging from 207 to 219 m a.s.l., with slope
132 differences between adjacent stations ranging from 0 to 6.4% (Fig. 1d). These topographic
133 variations likely influence local hydrological conditions and vegetation distribution. The relatively
134 even spacing of the stations enables detailed representation of these changes and allows
135 comprehensive analysis of the effects of landscape heterogeneity on groundwater flow paths,
136 inflow rates, and the associated input of CO₂ into streams.

137 2.2 Fieldwork and laboratory measurements

138 To cover seasonal variability under constraining hydrological conditions, stream water was
139 sampled every second week from 24th of April to 23rd of September 2020, resulting in 13 sampling
140 campaigns. During each campaign, stream stations were sampled on the same day, progressing
141 from downstream to upstream. Samples were collected within a three-hour window (10:00 –
142 13:00h) to minimise the potential influence of the time of day.

143 For CO₂ analysis, 4 mL of stream water was sampled just below the water surface and
144 injected into 22 mL gastight, acid-washed glass vials that had been flushed with N₂ at atmospheric
145 pressure and spiked with 20 µL of 4% HCl to convert all inorganic C species to CO₂ (Klaus et al.,
146 2018). The vial headspace was analysed for CO₂ partial pressure using a gas chromatograph (GC)
147 (Clarus 500, PerkinElmer Inc., USA). Gas mixtures containing known concentrations of CO₂ (410
148 and 9400 ppm) were prepared, stored, and analysed alongside each batch of samples as standards.
149 Triplicate samples of the standards yielded gas partial pressures within a 2% coefficient of
150 variation. The measured headspace partial pressures (ppm) were converted to molar concentrations



151 according to the ideal gas law, Henry's law and the temperature-dependent solubility of CO₂
152 (Klaus et al., 2018). As sample acidification shifts the carbonate equilibrium towards CO₂, some
153 of the measured headspace CO₂ may have resulted from other inorganic C species in the sample
154 water. Therefore, we calculated the original CO₂ concentration in the water from the measured vial
155 headspace CO₂ concentration using carbonate equilibrium reaction equations that account for the
156 effects of pH and water temperature (Stumm & Morgan, 1995). On average, we found that $98.2 \pm$
157 0.7% of the dissolved inorganic C (DIC) was present in the form of CO₂ at an average pH of $4.7 \pm$
158 1.0 (Hauptmann et al., in revision). The detection limit for DIC was $0.3 \mu\text{M}$, based on the water-
159 headspace volume ratio used.

160 For ²²²Rn concentrations, stream water samples were collected just below the water surface
161 into 2-L polyethene terephthalate (PET) soda bottles using a submersible pump to minimize water-
162 air contact and prevent ²²²Rn degassing, while avoiding headspace. Once in the laboratory, ²²²Rn
163 concentrations in the stream water were measured using a DurrIDGE Inc. RAD7 electronic radon-
164 in-air monitor, which was coupled with the RAD7 soda bottle aerator kit accessory. In a closed-
165 loop system, air was bubbled through the water samples for 40 minutes to reach equilibrium and
166 the ²²²Rn concentration was quantified through 15 counting cycles, each lasting 10 minutes.
167 Simultaneously, water sample temperature was measured and recorded to determine the air-water
168 partition coefficient. The ²²²Rn in the water was then calculated from the measured ²²²Rn
169 concentration in the air. This calculation considered the volumes of air and water in the system,
170 the water temperature during the measurement, the ambient ²²²Rn concentration in the air, and the
171 partitioning of ²²²Rn between air and water. The calculation also adjusted for water temperature
172 (Schubert et al., 2012). Additionally, corrections were made for the radioactive decay occurring
173 between the sampling and the subsequent analysis of ²²²Rn concentrations.

174 Groundwater ($n = 56$) was collected in eight PVC wells (Unoson Environment AB,
175 Mölnlycke, Sweden, 25x32 mm in diameter), installed approximately 3 m from the stream to
176 characterize the regional aquifers. The wells were arranged in four nests at 47, 74, 139, and 147 m
177 (G1, G3, G5, and G6, respectively) from the uppermost stream segment close to the mire (see Fig.
178 1b). Each nest contained two wells, with screenings in the bottom 10 cm, which allowed the inflow
179 of relatively shallow (0.75 – 0.90 m) and deep (1.15 – 1.30 m) groundwater, representing the Bs
180 and C horizon, respectively. The intakes were below the groundwater table throughout the
181 sampling period (Klaus et al., 2024). The wells were flushed the day before sampling to ensure
182 complete groundwater renewal. The groundwater was then pumped using a peristaltic pump and
183 sampled as the surface water, as described above. For ²²²Rn analysis, 10 mL of filtered ($0.45 \mu\text{m}$)
184 groundwater was collected and transferred directly to 20 mL polyethylene vials prefilled with
185 10 mL of high-efficiency liquid scintillator cocktail (Cable & Martin, 2008). ²²²Rn concentrations
186 in groundwater were analysed using an ultra-low level liquid scintillation counter (Quantulus



1220) with alpha-beta discrimination counting (background of 0.02 – 0.07 cpm; efficiency of 3.0 ± 0.2). The count rate of the measured sample was calculated from the start of measurement, taking into account the half-life of ^{222}Rn . For groundwater CO_2 analyses, we followed the procedure described in detail by (Klaus et al., 2024). Briefly, 10 mL of soil air that was in equilibrium with the groundwater was sampled from gas-permeable soil gas probes installed at the same locations and depths as the groundwater well intakes. We injected the air into pre-evacuated glass vials and analysed the partial pressure of CO_2 using a gas chromatograph (Clarus 580, PerkinElmer Inc., USA). To characterise the concentration of the gas in the groundwater end-member, we selected groundwater samples collected under conditions where groundwater flow was directed towards the stream ($n = 42$). This selection ensures that the samples accurately represent the contribution of groundwater flow chemistry. We inferred the direction of groundwater flow using Darcy's law based on manual groundwater level measurements taken at each sampling occasion at the wells sampled for ^{222}Rn , and at additional wells located 3 m from the ^{222}Rn sampling wells, i.e. 6 m from the stream (Klaus et al. 2024).

Stream discharge was estimated at five stations (S0, S4, S8, S13, and S18) (Fig. 1b) based on salt slug injections (Hauptmann et al., in revision). For the intermediate stations, ordinary least squares (OLS) regression was used to estimate the downstream increase in discharge (Hauptmann et al., in revision). The gas transfer velocity k was estimated by recording ambient sound recorded 30 cm above the stream surface using a handheld stereo audio recorder (Tascam DR-05X, TEAC Corporation, Santa Fe Springs, CA, USA), in accordance with published methodology (Hauptmann et al., in revision; Klaus et al., 2019). Ancillary parameters, including water temperature (T), temperature-specific conductivity (SPC), and air pressure, were measured *in situ* at the five stations with salt slug injections using a calibrated handheld water monitor (Yellow Springs Instruments ProSolo, Xylem Inc., Washington, DC, USA). Stream water samples for pH were collected without air bubbles in PVC bottles and kept cold upon return to the laboratory. We measured the pH using a benchtop meter (Mettler Delta 340) fitted with a pH Sensor (InLab® Power electrode, Mettler Toledo, Columbus, Ohio, United States). The mean depth and width of the stream segments between the stations were determined by averaging three measurements taken with a meter rod.

In autumn 2019, bulk mineral soil samples were collected from the same depths as the groundwater well intakes at the groundwater well sites using the core method and a volumetric cylinder (200 cm³). These samples were weighed and dried to calculate dry bulk density. We derived porosity from bulk density, assuming a solid mass density of 2.65 g cm⁻³, as verified by the pycnometer method (Blake & Hartge, 1986). The remaining soil samples were reserved for incubation experiments (Chanyotha et al., 2014; Corbett et al., 1998) to determine the diffusive ^{222}Rn input from the underlying soil, as well as the ^{222}Rn concentration in the groundwater.



Sediment samples were placed in 0.5 L PET bottles containing a known volume of Milli-Q water. These bottles were then measured using a RAD7 electronic radon-in-air monitor coupled with a RAD7 soda bottle aerator kit accessory, which ran 48 two-hour cycles. The rate of ^{222}Rn diffusion from the sediment (F_{diff}) was derived from the linear gradient obtained by plotting ^{222}Rn concentrations in air against time for the first seven hours of the experiment (Chanyotha et al., 2014). To determine the ^{222}Rn concentration in groundwater, approximately 200 g of dry sediment was placed in 0.5 L PET bottles, and the remaining volume was filled with Milli-Q water. All bottles were hermetically sealed and stored for 21 days, being periodically shaken. The ^{222}Rn concentration in groundwater was calculated as:

$$C_{gw} = C_{incubation} \frac{R_{lab}}{R_{field}} \quad (1)$$

where C_{gw} is the measured ^{222}Rn concentration [Bq m^{-3}], and R_{lab} and R_{field} are ratios of volume of water to sediment in the bottle (lab) and in the field (which is function of the porosity), respectively (Stieglitz et al., 2013). These parameters were incorporated into the ^{222}Rn mass to estimate groundwater inflow rates discharging into the study stream (see section 2.3).

2.3 Groundwater inflow rates and associated inputs of CO_2

Quantitative estimates of groundwater inflow rates were based on solving a mass balance equation that considered all sources of ^{222}Rn (i.e., advective groundwater flow, diffusive flux from bottom sediments, and production by its parent nuclide ^{226}Ra) and all sinks (i.e., radioactive decay in the water column and losses to the atmosphere). In a continuous-flow aquatic system that is not significantly affected by tributaries and is in steady state, a one-dimensional (1-D) mass balance model for the input of ^{222}Rn concentration ($[\text{Bq m}^{-3}]$) along a stream reach Δx_i can be written as:

$$\frac{d}{dx} (Q_i C_i) \Delta x_i \approx Q_{i-1} C_{i-1} - Q_i C_i = Q_{gw,i} C_{gw,i} + F_{diff} A_i + \lambda V_i C_{Ra,i} - F_{atm} A_i - \lambda V_i C_i \quad (2)$$

where Q_{i-1} and Q_i are the stream discharge [$\text{m}^3 \text{d}^{-1}$] at the upstream and downstream end of the stream section i ; C_{i-1} and C_i [Bq m^{-3}] are the ^{222}Rn concentrations in the upstream and downstream segment, respectively; $Q_{gw,i}$ [$\text{m}^3 \text{d}^{-1}$] is the advective groundwater inflow discharging to the studied stream section i ; $C_{gw,i}$ [Bq m^{-3}] is the ^{222}Rn concentration in the groundwater; F_{diff} is the molecular diffusion flux of ^{222}Rn from underlying sediments [$\text{Bq m}^{-2} \text{d}^{-1}$]; $C_{Ra,i}$ [Bq m^{-3}] is the ^{226}Ra concentration in the stream segment; F_{atm} [$\text{Bq m}^{-2} \text{d}^{-1}$] is the ^{222}Rn degassing to the atmosphere; λ is the ^{222}Rn decay constant [d^{-1}]; and A_i [m^2] and V_i [m^3] are the area and the volume of the studied stream segment, respectively. We acknowledge that the hyporheic flux of ^{222}Rn was assumed to be primarily mixed with ^{222}Rn inputs from shallow groundwater in the floodplain. Consequently, hyporheic water exchange is included in the total groundwater inflow flux to the stream. Evaporative losses of ^{222}Rn were considered negligible due to their extremely low rate in comparison to the gas transfer velocity of ^{222}Rn (Cook, 2015).



Equation (1) was used to estimate the flux of ^{222}Rn supplied to the stream compartment via groundwater ($F_{gw,i} = Q_{gw,i}C_{gw,i}$ [Bq d⁻¹]). The uncertainties associated with $F_{gw,i}$ were estimated deterministically by propagating the uncertainties of the individual terms in Equation 1. Using measurements of groundwater endmembers, we converted the ^{222}Rn fluxes supplied by groundwater ($F_{gw,i}$) into specific groundwater discharge (q_{gw} , [m d⁻¹]) and volumetric discharge (Q_{gw} , [m³ d⁻¹]) based on a Monte Carlo analysis. To achieve this, we generated 1000 $F_{gw,i}$ values for each stream segment based on a normal distribution and the calculated $F_{gw,i}$ and its uncertainty. Groundwater inflow rates ($Q_{gw,i}$) were then calculated by dividing the $F_{gw,i}$ values by the ^{222}Rn concentration in the groundwater ($C_{gw,i}$). In this study, we report specific groundwater inflow rates [m d⁻¹] instead of volumetric discharge [m³ d⁻¹] to enable direct comparison across stream segments of varying sizes, as segment dimensions inherently influence volumetric discharge. Finally, groundwater inflow rates were converted to groundwater-derived inputs of CO₂ using the measured concentrations of CO₂ in the groundwater end-members. Negative values of groundwater inflow rates and CO₂ inputs were considered as zero. The variability of groundwater inflow rates and derived CO₂ inputs was assessed by calculating the coefficient of variation (CV).

2.4 Stream CO₂ emissions and downstream export

To evaluate the importance of groundwater inflows in controlling CO₂ dynamics in the stream, we quantified total CO₂ losses through the two primary pathways (atmospheric emission and downstream export) and compared the magnitude of these with the contribution of groundwater.

^{222}Rn and CO₂ emissions across the water-air interface ([Bq m⁻² d⁻¹] for ^{222}Rn , [mg C m⁻² d⁻¹] for CO₂) were estimated using Fick's first law of gas diffusion:

$$F_{atm} = k_{gas}(C_{gas,i} - C_{gas,air}) \quad (3)$$

where k_{gas} [m d⁻¹] is the gas transfer velocity for the corresponding gas at the measured temperature, $C_{gas,i}$ and $C_{gas,air}$ ([Bq m⁻³] for ^{222}Rn , and [g C m⁻³] for CO₂) are the measured gas molar concentrations in the stream, and the theoretical concentrations in the stream if it was in equilibrium with the atmosphere, respectively, determined with the Henry's constant ($C_{CO_2,i} = 17$ μM at 20°C). The concentration of ^{222}Rn in the air was ignored because it was at least one order of magnitude lower than in the stream and groundwater.

Gas transfer velocity (k_{gas}) was estimated using the empirical equation of Macintyre et al. (1995):

$$k_{gas} = k_{600} \left(\frac{Sc}{600} \right)^{-0.5} \quad (4)$$

where Sc is the Schmidt number for the corresponding gas at the specific temperature (Sc is divided by 600 to normalize to CO₂ at 20°C) (Wanninkhof, 2014). This conversion accounts for the effects



290 of gas-specific diffusivity on air-water gas exchange but ignores the potential effects of gas
291 solubility on bubble-mediated gas exchange. Solubility effects only occur under sufficiently long
292 bubble residence times and were likely negligible in our stream as validated by previous work in
293 stream channels with similar hydraulic conditions (Klaus et al., 2022).

294 The standardised gas exchange velocity (k_{600}) was inferred at each stream reach using sound
295 spectral analysis (Klaus et al., 2019) from the sound pressure level spectrum caused by bubbles in
296 riffles and steps. Continuous estimates of discharge (Q , [L s⁻¹]) were used to model continuous k_{600}
297 based on the sampling station-specific linear relationship between Q and k_{600} (Hauptmann et al., in
298 revision).

299 We calculated the downstream CO₂ export [g CO₂ m⁻² d⁻¹] for each stream segment by
300 multiplying the discharge rate by the concentration of CO₂ at the downstream end of the stream
301 segment.

302 2.5 Statistics

303 The manuscript reports the median and the 25th and 75th percentiles of the estimated values
304 for stream and groundwater CO₂ and ²²²Rn concentrations, groundwater inflow rates, inputs of CO₂
305 through groundwater, downstream CO₂ export, and atmospheric CO₂ emissions. Differences in gas
306 concentrations between water sources (stream and groundwater), and spatial and seasonal
307 variations in gas concentrations and fluxes were analysed using analysis of variance (ANOVA),
308 followed by the Tukey-Kramer HSD post hoc test to identify differences between groups. Data
309 were log₁₀-transformed where necessary to meet assumptions of normality and homoscedasticity.
310 Test results were considered statistically significant at $p < 0.05$. All analyses were conducted using
311 the package ‘stats’ in R software (version 2023.12.1+402; R Core Team, 2023).

312 3 Results

313 3.1 Stream discharge and geochemical properties

314 3.1.1 Stream discharge

315 Measurements of stream discharge covered a wide range of hydrological conditions from
316 the snowmelt period (April and May) to summer base flow (July and August), including rain events
317 in July (see Appendix, Fig. S1). During the study period, discharge obtained through manual
318 measurements (April-May) varied from 0.80 to 41 L s⁻¹ (median 2.6 L s⁻¹, interquartile range (IQR):
319 1.4 – 13 L s⁻¹). Base-flow conditions were observed in mid-June and late August, with a median
320 discharge of 1.29 L s⁻¹ (IQR: 1.23 – 1.39 L s⁻¹). As indicated by elevated groundwater levels (Fig.
321 S1b), high-flow conditions prevailed in early May, with a discharge peak of 37.5 L s⁻¹ (IQR: 36.4
322 – 38.1 L s⁻¹). Elevated groundwater levels in July and August also reflected a secondary discharge
323 peak at the end of July (13.4 L s⁻¹, IQR: 12.6 – 14.0 L s⁻¹), associated with rain events (Fig. S1c).



3.1.2 Stream geochemical properties

Throughout the season and across all stations, the stream was CO₂ supersaturated relative to the atmosphere (Fig. 2a). Concentrations of CO₂ in the stream ranged from 54 to 450 μM (174 μM, IQR: 145 – 214 μM). Maximum CO₂ concentration was found upstream (S1), adjacent to the mire (329 μM, IQR: 231 – 376 μM). Subsequently, CO₂ concentrations decreased downstream until reaching almost constant values at the downstream stations (S14 and S15: 138 μM, IQR: 125 – 150 μM). In the lowermost section of the studied stream reach, CO₂ concentrations increased slightly (S16- S18: 152 μM, IQR: 138 – 184 μM).

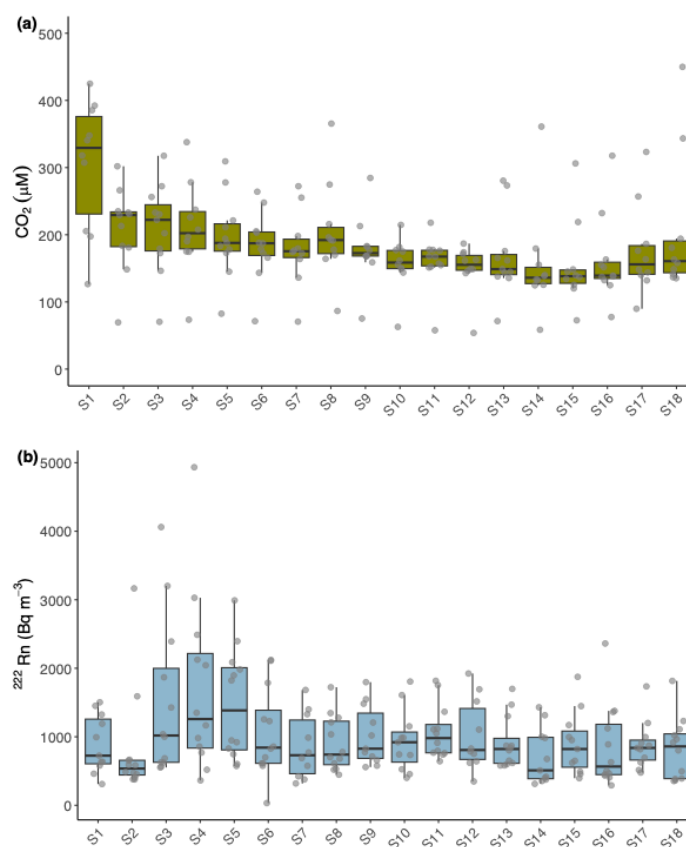


Figure 2: Boxplots showing concentrations of (a) CO₂ [μM] and (b) ²²²Rn [Bq m⁻³] along the stream reach. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile, with the solid line inside the box indicating the median value. Whiskers extend



to the most extreme data points within 1.5 times the IQR from the upper and lower quartiles.
 All individual observations used to construct the boxplots are plotted as grey circles.

333

334 The concentrations of ^{222}Rn in the stream water ranged from 32 to 4934 Bq m⁻³ (827 Bq
 335 m⁻³, IQR: 581 – 1311 Bq m⁻³) (Fig. 2b). The ^{222}Rn concentration increased slightly in the stream
 336 between stations S1 and S4, reaching a maximum of 1259 Bq m⁻³ (IQR: 835 – 2216 Bq m⁻³).
 337 Downstream of station S4, the concentration of ^{222}Rn decreased and stabilised at a constant value
 338 of 827 Bq m⁻³ (IQR: 590 – 1229 Bq m⁻³) along the studied stream reach. Over time, concentrations
 339 of ^{222}Rn correlated with CO₂ concentrations at the highest (S1 – S5) ($p < 0.041$, $R^2 = 0.37 - 0.65$)
 340 and lowest (S15 – S18) stream segments ($p < 0.04$, $R^2 = 0.39 - 0.61$) (Fig. S2), suggesting a
 341 consistent relationship between these two variables across different stream locations and
 342 conditions.

343 During the study period, we observed high temporal variability in CO₂ and ^{222}Rn
 344 concentrations in the stream water (Fig. 3). CO₂ concentrations were highest in early July (293
 345 µM, IQR: 257 – 318 µM) and at the end of August (252 µM, IQR: 214 – 278 µM) (Fig. 3a).
 346 Similarly, ^{222}Rn concentrations were highest at the beginning of July (1816 Bq m⁻³, IQR: 1631 –
 347 2299 Bq m⁻³), with a secondary peak at the end of August (1144 Bq m⁻³, IQR: 936 – 1396 Bq m⁻³)
 348 (Fig. 3b), concurrent with the peaks in CO₂ concentrations.

349 3.2 Groundwater geochemical properties

350 CO₂ concentrations in groundwater (1453 µM, IQR: 1202 – 1824 µM) were an order of
 351 magnitude higher than in stream water (Fig. S3a). A one-way ANOVA revealed a significant effect
 352 of well on CO₂ ($F = 3.047$, $p = 0.0406$), with higher concentrations found in well G6 than in well
 353 G3. Wells G1 and G5 had intermediate concentrations, not differing significantly from either G6
 354 or G3. Dissolved CO₂ in groundwater varied across months (ANOVA, $F = 3.11$, $p = 0.0154$, Fig.
 355 S3c). Concentrations were lowest in July (906 µM, IQR: 666 – 1257 µM), intermediate in spring
 356 (April and May: 1265 µM, IQR: 1142 – 1463 µM), and highest in late autumn (September–
 357 October: 1652 µM, IQR: 1470 – 2091 µM).

358 ^{222}Rn concentrations in groundwater (3591 µM, IQR: 1660 – 5525 µM) were at least three
 359 times higher than the ^{222}Rn concentration in the stream (Fig. S3b). Concentrations of ^{222}Rn in
 360 groundwater were lower in G6 than in the other wells (ANOVA, $F = 4.818$, $p = 0.0088$). In contrast
 361 to CO₂, ^{222}Rn concentrations did not vary throughout the sampling season (ANOVA, $F = 1.182$, p
 362 $= 0.35$, Fig. S3d). The anomalously low ^{222}Rn concentrations in well G6, together with Darcy's
 363 law estimates, suggest stream water infiltration rather than groundwater discharge. We excluded
 364 this well from the analyses as it does not represent the groundwater source of the study stream.



365

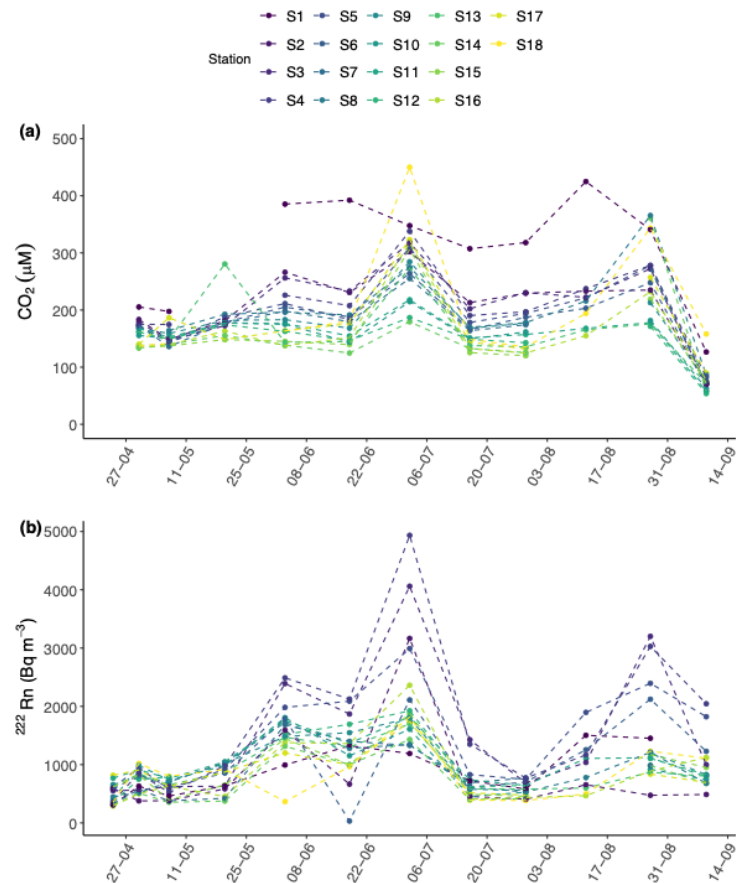


Figure 3: Temporal variation of (a) CO₂ and (b) ²²²Rn concentration in the stream during the study period (dates shown as DD-MM). Different colors represent different stations.

366

367 **3.3 Groundwater inflow rates and their significance to CO₂ emissions and export**

368 **3.3.1 Groundwater inflow rates**

369 The rate at which groundwater flowed into the stream varied between different stream
370 segments and at different times of the year, ranging from 0.00 to 31.5 m d⁻¹ (0.281 m d⁻¹, IQR: 0.00
371 – 2.58 m d⁻¹) (Fig. 4). For comparison purposes, the groundwater flux estimated from the difference
372 in discharge between upstream and downstream stations ($Q_i - Q_{i-1}$) ranged from 0.245 to 5.12 m
373 d⁻¹. Notably, the median inflow derived from the ²²²Rn mass balance (0.281 m d⁻¹) was close to the
374 lower bound of the discharge-based estimates (0.245 m d⁻¹). This alignment with the minimum



375 value reflects the conservative nature of our methodology. Assuming an average stream width of
376 36 cm and a length of 20 m per stream segment, the average groundwater discharge rate
377 corresponds to a volumetric flux of $2.02 \text{ m}^3 \text{ d}^{-1}$, which is at the lower end of the range obtained
378 from the discharge data (IQR: $1.63 - 11.7 \text{ m}^3 \text{ d}^{-1}$).

379 We identified three distinct segments along the stream with significant groundwater inputs
380 (S1-S4, S8-S11 and S14-S18, see Fig. 4a). These segments were classified as gaining reaches when
381 the estimated groundwater flow (Q_{gw}) was positive, so that only net groundwater inflows were
382 considered. In this way, the selected segments represent areas with consistently high groundwater
383 inflows. The upstream segment (S1-S4) recorded the highest groundwater inflow rates, with a
384 median value of 1.66 m d^{-1} (IQR: $0.00 - 5.29 \text{ m d}^{-1}$). Station S2 showed the highest groundwater
385 inflow rate, with 7.69 m d^{-1} (IQR: $3.74 - 10.6 \text{ m d}^{-1}$). The intermediate (S8 – S11) and downstream
386 (S14 – S18) segments showed lower groundwater contributions, with inflow rates of 0.350 m d^{-1}
387 (IQR: $0.00 - 1.97 \text{ m d}^{-1}$) and 1.01 m d^{-1} (IQR: $0.225 - 2.62 \text{ m d}^{-1}$), respectively. Conversely, stream
388 segments S5-S7 and S12-S13 showed no detectable groundwater inflows during most sampling
389 campaigns. Spatial patterns in groundwater inflow rates suggest a dependence on landscape
390 characteristics, particularly slope. Linear regression analysis revealed a significant relationship
391 between groundwater inflow rates and slope at stations influenced by groundwater ($F = 5.372$, $p =$
392 0.0407), with slope explaining 33% of the variation in inflow rate (see Fig. S4).

393 The upstream segment S1-S4 exhibited a median value of CV of 135%, whereas the
394 intermediate (S8-S11) and downstream (S14-S18) segments showed higher variability, with
395 respective CVs of 167% and 183%. These relatively high CV values reflect the temporal variability
396 of groundwater contribution across all segments. Similarly, individual stations showed a wide
397 range of variability: S2 and S10 had the lowest CVs (74% and 95%, respectively), while S1, S9,
398 and S15 had the highest (197%, 198%, and 240%, respectively). Despite differences in median
399 groundwater inflow rates, the consistently high CVs across sections and stations indicate that,
400 although recurrent, groundwater inputs were subject to strong temporal fluctuations throughout the
401 sampling period. At the stations where groundwater inflows were detectable, we observed a trend
402 towards higher values in May, with groundwater inflows of 2.24 m d^{-1} (IQR: $0.00778 - 4.88 \text{ m d}^{-1}$,
403 Fig. 4b). A secondary increase in groundwater inflow rates was observed at the end of July and
404 the beginning of August, with values of 0.44 m d^{-1} (IQR: $0.00 - 2.86 \text{ m d}^{-1}$).

405

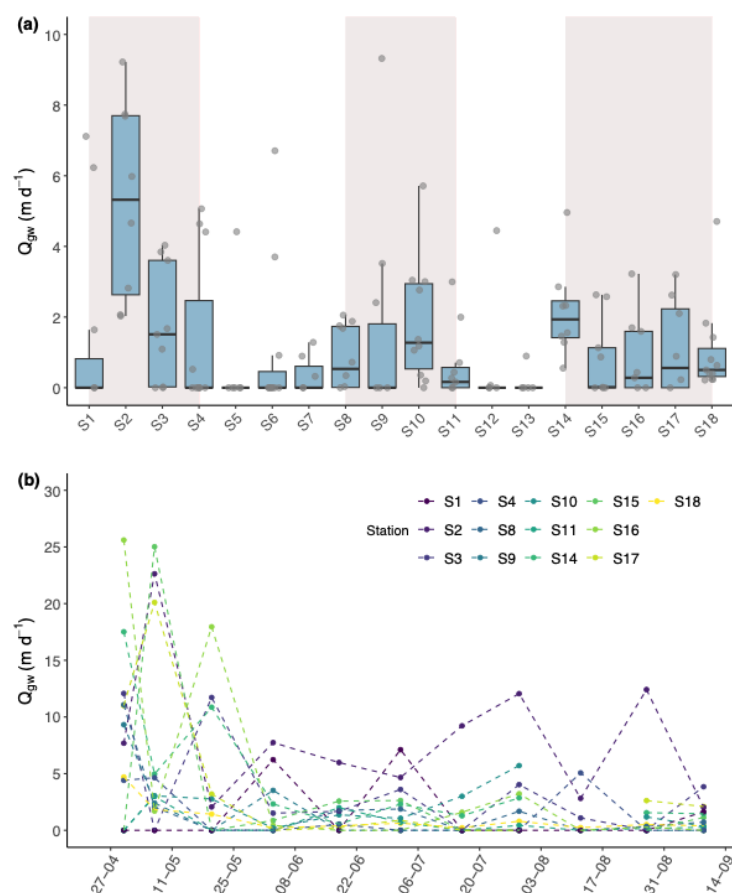


Figure 4: (a) Groundwater inflow rates along the stream reach. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile. The solid line inside the box indicates the median value. Whiskers extend to the most extreme data points within 1.5 times the IQR of the upper and lower quartiles. The shaded areas indicate stations where groundwater inflows were notably present. All individual observations used to construct the boxplots are plotted as grey circles. (b) Temporal variations in the groundwater inflow rates at stations with significant groundwater inflow; dates are shown in DD-MM format.

406

407 3.3.2 Stream CO₂ emissions and CO₂ downstream export

408 The stream consistently emitted CO₂ into the atmosphere (Fig. 5a), with emissions ranging
 409 from 0.3 to 25.1 g C m⁻² d⁻¹ (3.0 g C m⁻² d⁻¹, IQR: 1.9 – 4.9 g C m⁻² d⁻¹) across all stations and
 410 throughout the study period. The highest CO₂ emissions were found at the topmost station (S1),
 411 with 18.6 g C m⁻² d⁻¹ (IQR: 17.9 – 21.9 g C m⁻² d⁻¹). Moderately elevated CO₂ emissions were



412 found at S2 and S16, with $7.4 \text{ g C m}^{-2} \text{ d}^{-1}$ (IQR: $6.4 - 8.5 \text{ g C m}^{-2} \text{ d}^{-1}$) and $5.6 \text{ g C m}^{-2} \text{ d}^{-1}$ (IQR: 3.7
413 $- 8.8 \text{ g C m}^{-2} \text{ d}^{-1}$), respectively. A gradual decline in CO_2 emissions was observed from S2 to S10,
414 followed by a subsequent increase in CO_2 emissions from S11 to S16. Further downstream of
415 station S16, CO_2 emissions decreased again, reaching $2.2 \text{ g C m}^{-2} \text{ d}^{-1}$ (IQR: $2.1 - 2.6 \text{ g C m}^{-2} \text{ d}^{-1}$)
416 at the most downstream station (S18).
417

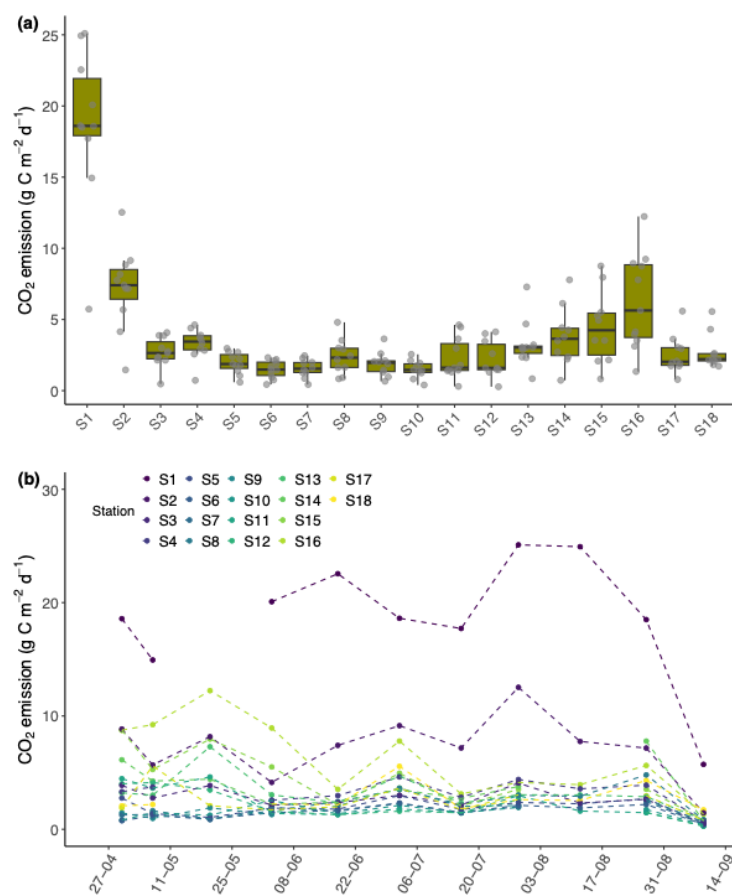


Figure 5: (a) Atmospheric emissions of CO_2 along the stream reach. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile, with the solid line inside the box indicating the median value. Whiskers extend to the most extreme data points within 1.5 times the IQR from the upper and lower quartiles. All individual observations used to construct the boxplots are plotted as grey circles. (b) Atmospheric emissions of CO_2 through the sampling season at the different stream segments.



CO₂ emissions were relatively stable throughout the sampling period, with consistently high emissions from late April to mid-August (2.6 g C m⁻² d⁻¹, IQR: 1.9 – 4.1 g C m⁻² d⁻¹) (Fig. 5b). Afterwards, a notable decline in CO₂ emissions was observed, with a tendency of values in September being lower (0.7 g C m⁻² d⁻¹, IQR: 0.4 – 0.8 g C m⁻² d⁻¹) than earlier in the year.

Downstream CO₂ export ranged from 9.2 to 864 g C m⁻² d⁻¹ (Fig. 6a). The median value for all stream segments was similar ($F = 0.03$, $p = 1$), at 76 g C m⁻² d⁻¹. Downstream CO₂ export fluctuated throughout the sampling season (Fig. 6b). During base-flow conditions between mid-June and mid-July, CO₂ export varied from 28 to 92 g C m⁻² d⁻¹ (43 g C m⁻² d⁻¹, IQR: 38 – 53 g C m⁻² d⁻¹). The highest amounts of CO₂ were exported downstream in early May, with a median value of 647 g C m⁻² d⁻¹ (IQR: 611 – 678 g C m⁻² d⁻¹). A second peak in downstream CO₂ export was observed at the end of July, with a median value of 330 g C m⁻² d⁻¹ (IQR: 296 – 355 g C m⁻² d⁻¹).

3.3.3. Groundwater CO₂ inputs to the stream

For stream segments with significant groundwater inflows, the CO₂ input via groundwater ranged from 0.00 to 535 g C m⁻² d⁻¹ (Fig. 7a). The median groundwater CO₂ inputs (13 g C m⁻² d⁻¹, IQR: 0.00 – 50 g C m⁻² d⁻¹) exceeded the median atmospheric CO₂ emissions from these stream segments (3.0 g C m⁻² d⁻¹, IQR: 1.9– 4.9 g C m⁻² d⁻¹) by up to a factor of 20. Groundwater-derived CO₂ inputs were of the same order of magnitude as the CO₂ exported downstream (76 g C m⁻² d⁻¹, IQR: 46– 300 g C m⁻² d⁻¹). This suggests that a substantial proportion of the CO₂ delivered by groundwater is transported downstream rather than being emitted into the atmosphere.

Groundwater CO₂ inputs showed strong temporal variability (Fig. S5). The highest CO₂ inflows were observed at the end of April, reaching a median value of 108 g C m⁻² d⁻¹ (IQR: 58 – 126 g C m⁻² d⁻¹). Inputs decreased towards the beginning of summer, but increased again in late July, reaching a median value of 136 g C m⁻² d⁻¹ (IQR: 46 – 175 g C m⁻² d⁻¹). During baseflow conditions, groundwater CO₂ inputs were consistently low, with median values of 10 g C m⁻² d⁻¹ (IQR: 7.1 – 18 g C m⁻² d⁻¹) in mid-July and 16 g C m⁻² d⁻¹ (IQR: 6.6 – 31 g C m⁻² d⁻¹) in late August.

The relative contribution of groundwater-derived CO₂ inputs to stream CO₂ export, reported as the median across stations for each sampling date, varied markedly over time (Fig. 7b). The highest contribution occurred in early September, with groundwater CO₂ inputs accounting for up to 100% of the total downstream CO₂ export. Substantial contributions were also observed during baseflow conditions in summer, with groundwater accounting for 44% and 23% of the total CO₂ export in mid-June and late August, respectively.

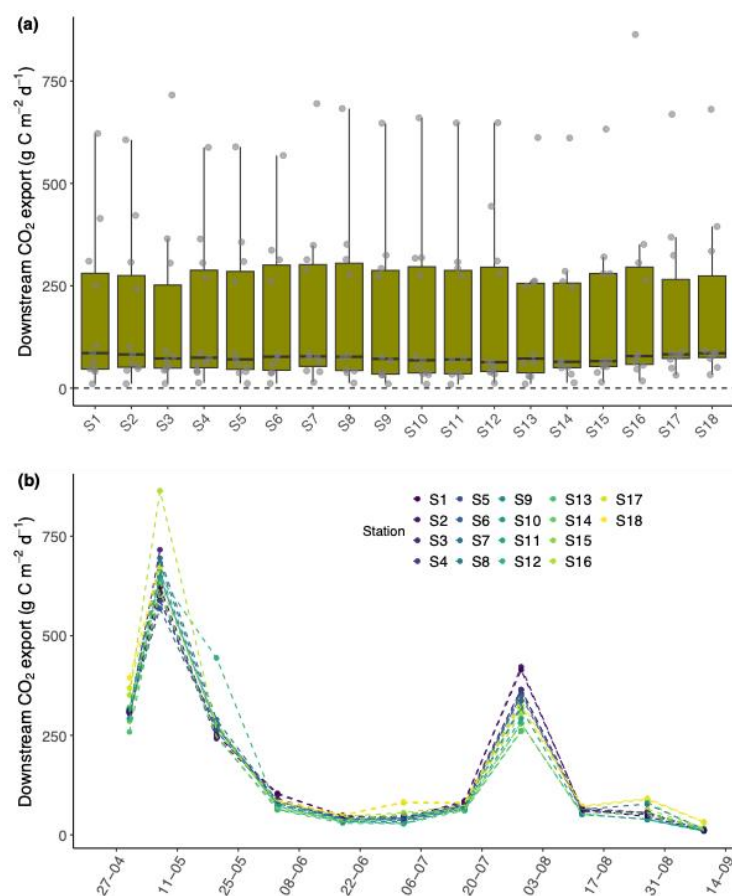


Figure 6: (a) Downstream CO₂ export across stream segments. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile, with the solid line inside the box indicating the median value. Whiskers extend to the most extreme data points within 1.5 times the IQR from the upper and lower quartiles. All individual observations used to construct the boxplots are plotted as grey circles. (b) Stream CO₂ export through the sampling season.

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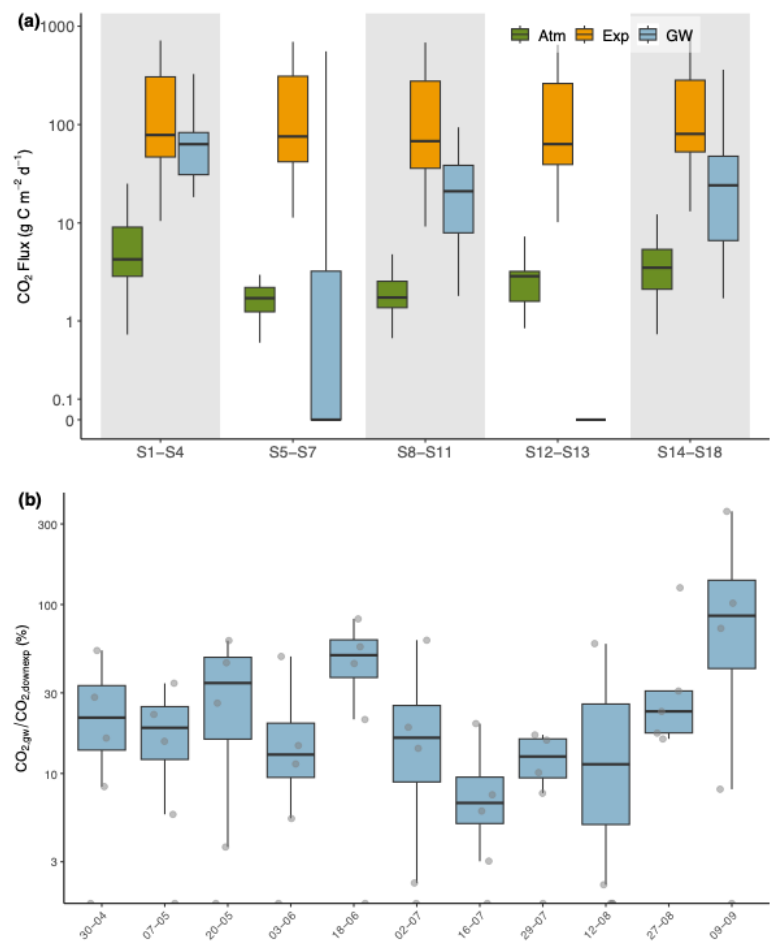


Figure 7. CO₂ fluxes in stream segments shown on a logarithmic scale. (a) Comparison of CO₂ fluxes via groundwater, atmospheric emissions, and downstream export. (b) Temporal variation in the relative contribution of groundwater CO₂ inputs to downstream CO₂ export along the stream. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile, with the solid line inside the box indicating the median value. Whiskers extend to the most extreme data points within 1.5 times the IQR from the upper and lower quartiles. All individual observations used to construct the boxplots in panel b) are plotted as grey circles.

453

454 **4 Discussion**

455 **4.1 Spatio-temporal variations of groundwater CO₂ inputs to boreal headwater streams**

456 **4.1.1 Spatial variations in groundwater CO₂ inputs**



Groundwater CO₂ inputs to the study stream showed spatial variability at the scale of tens of meters (Fig. 7a), which is consistent with previous observations in nearby boreal streams (Lupon et al., 2019b). However, after excluding one hydrogeochemically distinct well (identified a priori by an anomalous ²²²Rn signature), CO₂ concentrations did not differ significantly among wells (Fig. S3a). This indicates that the observed spatial heterogeneity is more likely driven by differences in groundwater inflow rates rather than by variation in riparian CO₂ production. This interpretation is further supported by the positive correlation between CO₂ and ²²²Rn concentrations in both upstream (S1 – S5) and downstream (S15 – S18) stations (Fig. S2), which highlights the effectiveness of ²²²Rn as a tracer of groundwater-derived CO₂ inputs. The observed spatial variability in groundwater inflows significantly affects reach-scale estimates of CO₂ evasion (Hotchkiss et al., 2015a; Lupon et al., 2019), emphasizing the need to account for such heterogeneity when quantifying stream C fluxes.

Spatial patterns in groundwater inflow rates appear to depend on landscape characteristics, particularly slope. Steeper areas tend to have higher inflow rates, likely due to stronger hydrological gradients promoting infiltration and subsurface channel flows (Leach et al., 2017; McGlynn & McDonnell, 2003). This pattern is further supported by the positive correlation observed between slope and groundwater inflow rates at high-inflow stations (see Fig. S4). In contrast, lower inflow rates were associated to more gentle slopes, highlighting the role of topography in shaping groundwater contributions to streams. This finding corroborates previous research on the role of groundwater inflows in groundwater-dependent ecosystems, suggesting that higher rates of groundwater typically occur where rivers or streams run adjacent to hills or flow through incised valleys (Cartwright & Gilfedder, 2015). However, the magnitude of groundwater inflows along the stream showed a considerable range of temporal variability as indicated by the coefficients of variation (CV). Notably, stream segments influenced by groundwater exhibited high CV values (~ 200%; S1, S8, S9, and S15), reflecting significant temporal fluctuations in groundwater inflows. This variability is likely caused by transient hydrological factors, including variable recharge rates, preferential flow paths, localized aquifer heterogeneities, and human impact such as ditching (Fig. 1b). These factors can cause groundwater inflows to fluctuate in magnitude and timing, which would increase the CV. Heterogeneity in groundwater inflows along the stream reach was also reflected in differences in water table depth among the monitoring wells (Fig. S1b), with mean depths varying up to a factor of four between wells. Together, these observations emphasize the spatial and temporal complexity of hydrological pathways and groundwater dynamics, highlighting the need for site-specific studies to more accurately capture the contribution of groundwater to stream CO₂ emissions.

Variations in soil composition along the stream reach may influence the availability of CO₂ for groundwater export, potentially contributing to the observed spatial patterns of groundwater



CO₂ inputs. Autotrophic root respiration and heterotrophic respiration of organic C stored in the riparian zone are recognised as the main sources of soil CO₂ and lateral transport to the stream (Campeau et al., 2019; Hope et al., 2004). In our study, however, we did not detect clear differences in CO₂ concentrations between groundwater wells, likely because the monitoring network had limited spatial coverage, being confined to ~ 200m of the stream corridor. A denser network of groundwater wells would be needed to better resolve potential small-scale heterogeneity in subsurface CO₂ production and transport along the stream corridor.

4.1.2 Temporal variations in groundwater CO₂ inputs

While spatial variability shaped the distribution of groundwater CO₂ inputs along the stream, temporal fluctuations were equally important in determining the magnitude and timing of these inputs. The highest groundwater CO₂ inputs were observed in late spring (late April- early May) (Fig. S5), with median values exceeding CO₂ emissions to the atmosphere (Fig. 5a). These peaks in groundwater CO₂ inputs were mainly caused by increased groundwater inflow rates driven by snowmelt (Fig. 4a) (Audrey Campeau et al., 2014; Dyson et al., 2011), rather than by elevated CO₂ concentrations in the groundwater. Reduced respiration during winter likely limited the accumulation of dissolved CO₂ in the groundwater, as reflected by the lower CO₂ concentrations found in May compared to those in summer and early autumn (Klaus et al., 2024) (Fig. S3c). Therefore, although snowmelt is usually linked with low CO₂ concentrations in groundwater, the substantial increase in water table levels and inflow rates during this period means that groundwater is a significant pathway for lateral CO₂ transfer. This emphasizes the need to consider not only CO₂ concentrations, but also hydrological dynamics when evaluating the role of groundwater in stream C cycling.

CO₂ inputs via groundwater were also relatively high in late summer and early autumn (Fig. S5), which coincided with precipitation events and associated increased stream discharge (see Fig. S1). This pattern is consistent with previous observations showing that intensive rainfall events recharge the groundwater system and enhance interactions between groundwater and surface water, likely through rapid infiltration and increased hydraulic connectivity between the aquifer and the stream. Groundwater recharge raises the water table (see Fig. S1b), thereby increasing the hydraulic head gradient between the groundwater and the stream. This, in turn, drives higher groundwater inflow rates (Cartwright & Gilfedder 2015) and reinforces the strong hydrological coupling between surface water and groundwater in the study area. Additionally, higher soil temperatures in summer compared to spring (Klaus et al., 2024) may accelerate the decomposition of soil organic matter, thereby increasing the production of dissolved OC (DOC) in soil porewater (Schelker et al., 2013). Root respiration during periods of peak primary production also contributes to elevated CO₂ concentrations in soil and groundwater (Högberg et al., 2001). Together, these processes may explain the higher CO₂ concentrations observed in groundwater during late summer



529 and autumn (Fig. S3c). The combination of elevated soil and groundwater CO₂ concentrations,
 530 alongside significant groundwater inflow following summer and early autumn rainfall events,
 531 results in substantial CO₂ inputs to the stream via groundwater. This mechanism is modulated by
 532 physical factors, such as stream morphology, sediment permeability, and precipitation, as well as
 533 biological factors such as primary production. Therefore, understanding these interactions is
 534 critical to understanding the role of groundwater in shaping CO₂ dynamics in headwater streams.
 535 This highlights the importance of considering not only hydrological processes, but also biological
 536 processes, when studying CO₂ production and export within the catchment, as these may vary over
 537 time.

538 **4.2 The magnitude and fate of groundwater CO₂ inputs**

539 We consistently observed higher CO₂ concentrations in groundwater than in stream water,
 540 which supports our hypothesis that groundwater inflows can serve as an important source of CO₂
 541 to headwater streams under conditions favouring subsurface transport. Similar CO₂ enrichments
 542 have been reported in the riparian groundwater of other boreal forests (Biehler et al., 2023; Lupon
 543 et al., 2019; Venkiteswaran et al., 2014). Groundwater CO₂ concentrations at our study site were
 544 consistent with (Venkiteswaran et al., 2014, Klaus et al. 2018) or at the upper end of those reported
 545 in nearby catchments (Lupon et al., 2019). These findings suggest that relatively small
 546 groundwater inflows can disproportionately impact a stream's CO₂ budget.

547 Results from the ²²²Rn mass balance indicate that groundwater inflow from the riparian zone
 548 primarily occurred at three main segments along the stream reach (see A4A). CO₂ inputs at these
 549 segments highlight the role of groundwater as a significant source of C to headwater streams, with
 550 inputs exceeding total CO₂ emissions by up to 20-fold (Fig. 7a). Median groundwater CO₂ input is
 551 comparable to values reported for a nearby catchment during the ice-free period (Lupon et al.,
 552 2019). These findings highlight the importance of groundwater for stream C budgets, particularly
 553 in systems with spatially focused inflows. While a portion of this CO₂ is likely evaded shortly after
 554 entering the stream (Öquist et al., 2009), the magnitude of inputs relative to emissions emphasizes
 555 that groundwater can substantially sustain in-stream CO₂ availability.

556 Not all CO₂ delivered via groundwater is immediately emitted to the atmosphere. A
 557 substantial fraction may be transported downstream (Hauptmann et al., in revision), where it can
 558 either contribute to CO₂ emissions further along the network or be utilized in in-stream processes
 559 (Hotchkiss et al., 2015). When averaged over the entire sampling season and limited to stream
 560 segments influenced by groundwater inflows, these inputs accounted for up to 100% of the total
 561 downstream CO₂ export. High-resolution spatial and temporal sampling revealed substantial
 562 variability, with up to a three-fold difference among stream segments and a ten-fold variation



563 across sampling dates, highlighting the dynamic and localized role of groundwater in shaping
 564 stream C fluxes.

565 **5 Conclusions**

566 This study highlights the critical role of groundwater inflow in transferring terrestrially derived
 567 CO₂ into boreal headwater streams and shaping stream C dynamics. While not all groundwater-
 568 derived CO₂ is immediately released into the atmosphere, our results indicate that a substantial
 569 fraction is transported downstream, where it can fuel further emissions along the stream continuum
 570 or be used in in-stream biological processes. The fate of this CO₂ (rapid atmospheric evasion,
 571 downstream export, or in-stream processing) depends on hydrological and biogeochemical
 572 controls, including gas exchange velocity, water depth, and travel time. Spatially, contributions
 573 from groundwater vary markedly at fine spatial scales (tens of meters) and are shaped by catchment
 574 characteristics such as stream slope, with additional modulation by preferential flow paths,
 575 localised aquifer heterogeneities, or variable recharge. Temporally, groundwater CO₂ inputs are
 576 regulated by hydrological processes (snow melt- and rainfall- driven recharge) and biological
 577 activity (e.g., soil respiration), which together control the production and transport of CO₂ from
 578 the riparian zone to the stream. Comprehensive assessments of the patterns and controls of stream
 579 CO₂ dynamics therefore require an evaluation of both the spatial and temporal variability of
 580 groundwater inflows, as well as downstream export, atmospheric emission, and biological activity,
 581 not only within the channel but also throughout the riparian corridor. This integrative
 582 understanding is particularly important in the context of global environmental change, as it
 583 improves our ability to predict how boreal headwater streams will respond to changing climate and
 584 hydrological conditions

585 **6 Supplement**

586 The supplement used in this article are publicly available at the Figshare Digital Repository via the
 587 following link: <https://doi.org/10.6084/m9.figshare.30501437> (Olid et al., 2025).

588 **7 Author contribution**

589 Conceptualization and methodology by DH, MK, JK, and CO; investigation and data curation by
 590 CO, DH and MK; formal analysis by CO; funding acquisition by JK, MK, and CO; resources by
 591 JK, MK and CO; visualization by CO and DH; writing – original draft preparation by CO; writing
 592 – review and editing by DH, MK, JK, and CO.

593 **8 Competing interests**

594 The authors declare that they have no competing interests.

595 **9 Acknowledgements**



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