



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

4

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)

12

13

14



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.

37

38



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



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

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

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

100 **2 Material and Methods**

101 **2.1 Study area**

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

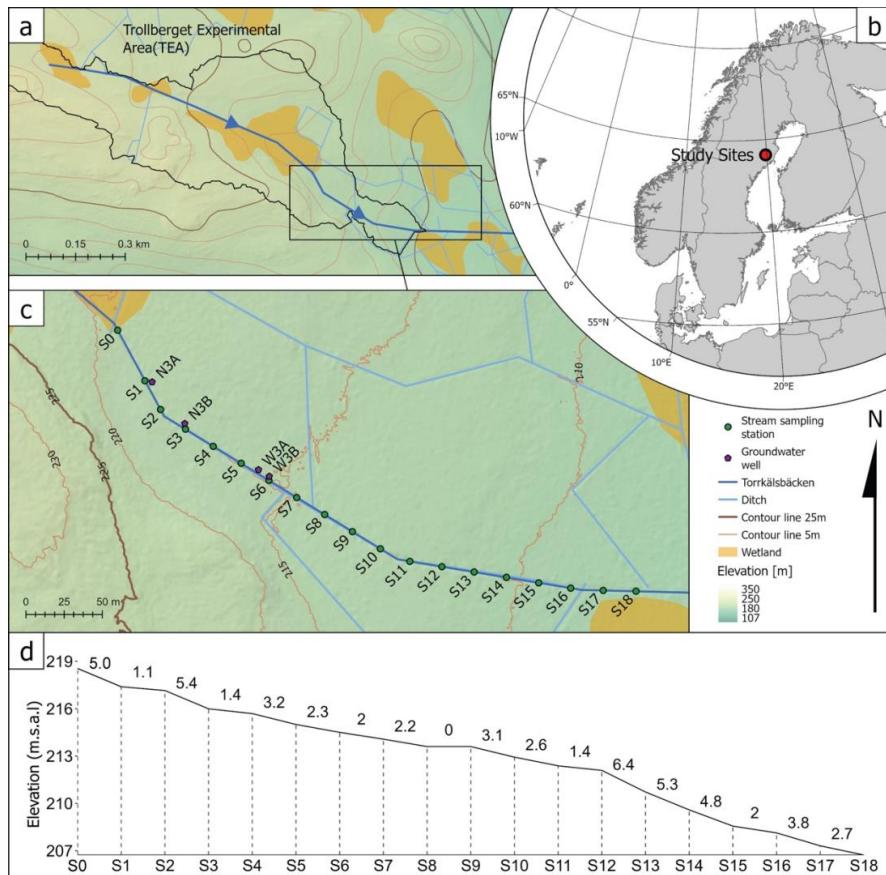


Figure 1: (a) Location of the Trollberget Experimental Area (TEA), (b) a close-up of the study reach within TEA, (c) relative location within northern Europe and d) Elevation profile (in m) and slope (%) along the sampling stations of the stream (Hauptmann et al., in revision). Locations of the outlet 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).

109

110 Forest growing on podzol developed in glacial till covers 87% of the Torrkälsbäcken
 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* spp.), and scattered occurrences of alder (*Alnus*
 113 *incana* (L.) Moench), aspen (*Populus tremula* L.), and willow (*Salix* spp.) in the riparian areas.
 114 The remaining 13% of the catchment is covered equally by open mire and forest on mire.
 115 Torrkälsbäcken 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 ±
157 0.7% of the dissolved inorganic C (DIC) was present in the form of CO₂ at an average pH of 4.7 ±
158 1.0 (Hauptmann et al., in revision). The detection limit for DIC was 0.3 µM, 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 µm)
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



187 1220) with alpha-beta discrimination counting (background of 0.02 – 0.07 cpm; efficiency of 3.0
188 ± 0.2). The count rate of the measured sample was calculated from the start of measurement, taking
189 into account the half-life of ^{222}Rn . For groundwater CO₂ analyses, we followed the procedure
190 described in detail by (Klaus et al., 2024). Briefly, 10 mL of soil air that was in equilibrium with
191 the groundwater was sampled from gas-permeable soil gas probes installed at the same locations
192 and depths as the groundwater well intakes. We injected the air into pre-evacuated glass vials and
193 analysed the partial pressure of CO₂ using a gas chromatograph (Clarus 580, PerkinElmer Inc.,
194 USA). To characterise the concentration of the gas in the groundwater end-member, we selected
195 groundwater samples collected under conditions where groundwater flow was directed towards the
196 stream (n = 42). This selection ensures that the samples accurately represent the contribution of
197 groundwater flow chemistry. We inferred the direction of groundwater flow using Darcy's law
198 based on manual groundwater level measurements taken at each sampling occasion at the wells
199 sampled for ^{222}Rn , and at additional wells located 3 m from the ^{222}Rn sampling wells, i.e. 6 m from
200 the stream (Klaus et al. 2024).

201 Stream discharge was estimated at five stations (S0, S4, S8, S13, and S18) (Fig. 1b) based
202 on salt slug injections (Hauptmann et al., in revision). For the intermediate stations, ordinary least
203 squares (OLS) regression was used to estimate the downstream increase in discharge (Hauptmann
204 et al., in revision). The gas transfer velocity k was estimated by recording ambient sound recorded
205 30 cm above the stream surface using a handheld stereo audio recorder (Tascam DR-05X, TEAC
206 Corporation, Santa Fe Springs, CA, USA), in accordance with published methodology
207 (Hauptmann et al., in revision; Klaus et al., 2019). Ancillary parameters, including water
208 temperature (T), temperature-specific conductivity (SPC), and air pressure, were measured *in situ*
209 at the five stations with salt slug injections using a calibrated handheld water monitor (Yellow
210 Springs Instruments ProSolo, Xylem Inc., Washington, DC, USA). Stream water samples for pH
211 were collected without air bubbles in PVC bottles and kept cold upon return to the laboratory. We
212 measured the pH using a benchtop meter (Mettler Delta 340) fitted with a pH Sensor (InLab®
213 Power electrode, Mettler Toledo, Columbus, Ohio, United States). The mean depth and width of
214 the stream segments between the stations were determined by averaging three measurements taken
215 with a meter rod.

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



223 Sediment samples were placed in 0.5 L PET bottles containing a known volume of Milli-Q water.
224 These bottles were then measured using a RAD7 electronic radon-in-air monitor coupled with a
225 RAD7 soda bottle aerator kit accessory, which ran 48 two-hour cycles. The rate of ^{222}Rn diffusion
226 from the sediment (F_{diff}) was derived from the linear gradient obtained by plotting ^{222}Rn
227 concentrations in air against time for the first seven hours of the experiment (Chanyotha et al.,
228 2014). To determine the ^{222}Rn concentration in groundwater, approximately 200 g of dry sediment
229 was placed in 0.5 L PET bottles, and the remaining volume was filled with Milli-Q water. All
230 bottles were hermetically sealed and stored for 21 days, being periodically shaken. The ^{222}Rn
231 concentration in groundwater was calculated as:

232
$$C_{gw} = C_{incubation} \frac{R_{lab}}{R_{field}} \quad (1)$$

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

237 **2.3 Groundwater inflow rates and associated inputs of CO₂**

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

244
$$\frac{d}{dx} (Q_i C_i) \Delta x_i \approx Q_{i-1} C_{i-1} - Q_i C_i = Q_{gw,i} C_{gw,i} + F_{diff} A_i + \lambda V_i C_{Ra,i} - F_{atm} A_i - \lambda V_i C_i \quad (2)$$

245 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
246 stream section i ; C_{i-1} and C_i [Bq m^{-3}] are the ^{222}Rn concentrations in the upstream and downstream
247 segment, respectively; $Q_{gw,i}$ [$\text{m}^3 \text{ d}^{-1}$] is the advective groundwater inflow discharging to the studied
248 stream section i ; $C_{gw,i}$ [Bq m^{-3}] is the ^{222}Rn concentration in the groundwater; F_{diff} is the molecular
249 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
250 concentration in the stream segment; F_{atm} [$\text{Bq m}^{-2} \text{ d}^{-1}$] is the ^{222}Rn degassing to the atmosphere; λ
251 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
252 stream segment, respectively. We acknowledge that the hyporheic flux of ^{222}Rn was assumed to
253 be primarily mixed with ^{222}Rn inputs from shallow groundwater in the floodplain. Consequently,
254 hyporheic water exchange is included in the total groundwater inflow flux to the stream.
255 Evaporative losses of ^{222}Rn were considered negligible due to their extremely low rate in
256 comparison to the gas transfer velocity of ^{222}Rn (Cook, 2015).



257 Equation (1) was used to estimate the flux of ^{222}Rn supplied to the stream compartment
258 via groundwater ($F_{gw,i} = Q_{gw,i}C_{gw,i}$ [Bq d $^{-1}$]). The uncertainties associated with $F_{gw,i}$ were
259 estimated deterministically by propagating the uncertainties of the individual terms in Equation 1.
260 Using measurements of groundwater endmembers, we converted the ^{222}Rn fluxes supplied by
261 groundwater ($F_{gw,i}$) into specific groundwater discharge (q_{gw} , [m d $^{-1}$]) and volumetric discharge
262 (Q_{gw} , [m 3 d $^{-1}$]) based on a Monte Carlo analysis. To achieve this, we generated 1000 $F_{gw,i}$ values
263 for each stream segment based on a normal distribution and the calculated $F_{gw,i}$ and its uncertainty.
264 Groundwater inflow rates ($Q_{gw,i}$) were then calculated by dividing the $F_{gw,i}$ values by the ^{222}Rn
265 concentration in the groundwater ($C_{gw,i}$). In this study, we report specific groundwater inflow
266 rates [m d $^{-1}$] instead of volumetric discharge [m 3 d $^{-1}$] to enable direct comparison across stream
267 segments of varying sizes, as segment dimensions inherently influence volumetric discharge.
268 Finally, groundwater inflow rates were converted to groundwater-derived inputs of CO $_2$ using the
269 measured concentrations of CO $_2$ in the groundwater end-members. Negative values of groundwater
270 inflow rates and CO $_2$ inputs were considered as zero. The variability of groundwater inflow rates
271 and derived CO $_2$ inputs was assessed by calculating the coefficient of variation (CV).

272 2.4 Stream CO $_2$ emissions and downstream export

273 To evaluate the importance of groundwater inflows in controlling CO $_2$ dynamics in the
274 stream, we quantified total CO $_2$ losses through the two primary pathways (atmospheric emission
275 and downstream export) and compared the magnitude of these with the contribution of
276 groundwater.

277 ^{222}Rn and CO $_2$ emissions across the water-air interface ([Bq m $^{-2}$ d $^{-1}$] for ^{222}Rn , [mg C m $^{-2}$
278 d $^{-1}$] for CO $_2$) were estimated using Fick's first law of gas diffusion:

$$279 \quad F_{atm} = k_{gas}(C_{gas,i} - C_{gas,air}) \quad (3)$$

280 where k_{gas} [m d $^{-1}$] is the gas transfer velocity for the corresponding gas at the measured temperature,
281 $C_{gas,i}$ and $C_{gas,air}$ ([Bq m $^{-3}$] for ^{222}Rn , and [g C m $^{-3}$] for CO $_2$) are the measured gas molar
282 concentrations in the stream, and the theoretical concentrations in the stream if it was in
283 equilibrium with the atmosphere, respectively, determined with the Henry's constant ($C_{CO2,i} = 17$
284 μM at 20°C). The concentration of ^{222}Rn in the air was ignored because it was at least one order of
285 magnitude lower than in the stream and groundwater.

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

$$287 \quad k_{gas} = k_{600} \left(\frac{Sc}{600} \right)^{-0.5} \quad (4)$$

288 where Sc is the Schmidt number for the corresponding gas at the specific temperature (Sc is divided
289 by 600 to normalize to CO $_2$ 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 CO_2 export [$\text{g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$] for each stream segment by
300 multiplying the discharge rate by the concentration of CO_2 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 CO_2 and ^{222}Rn concentrations, groundwater inflow rates, inputs of CO_2
305 through groundwater, downstream CO_2 export, and atmospheric CO_2 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 \log_{10} -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).



324 **3.1.2 Stream geochemical properties**

325 Throughout the season and across all stations, the stream was CO₂ supersaturated relative
326 to the atmosphere (Fig. 2a). Concentrations of CO₂ in the stream ranged from 54 to 450 µM (174
327 µM, IQR: 145 – 214 µM). Maximum CO₂ concentration was found upstream (S1), adjacent to the
328 mire (329 µM, IQR: 231 – 376 µM). Subsequently, CO₂ concentrations decreased downstream
329 until reaching almost constant values at the downstream stations (S14 and S15: 138 µM, IQR: 125
330 – 150 µM). In the lowermost section of the studied stream reach, CO₂ concentrations increased
331 slightly (S16- S18: 152 µM, IQR: 138 – 184 µM).

332

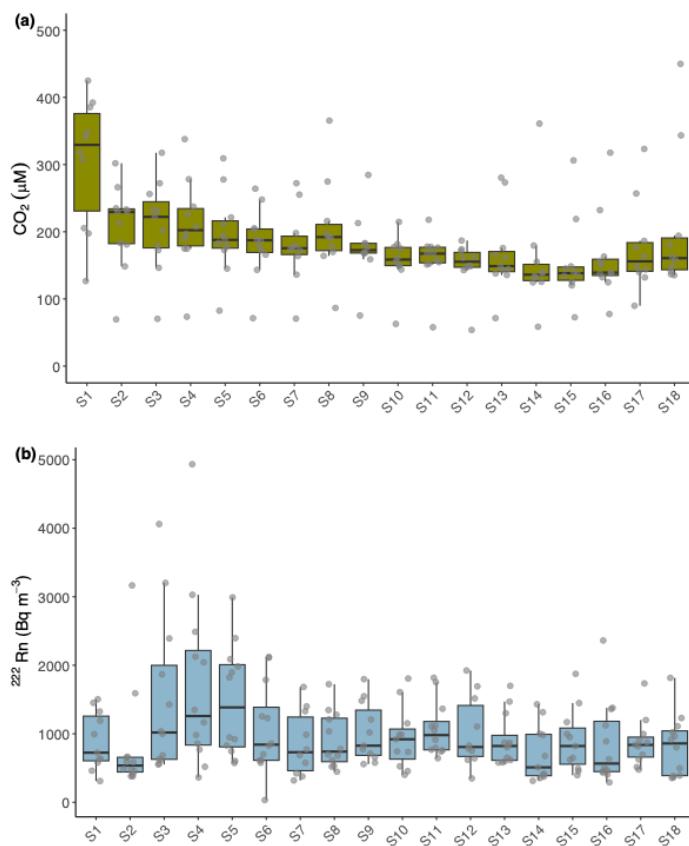


Figure 2: Boxplots showing concentrations of (a) CO₂ [µM] and (b) ²²²Rn [Bq m⁻³] along the stream reach. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile, with the solid line inside the box indicating the median value. Whiskers extend



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

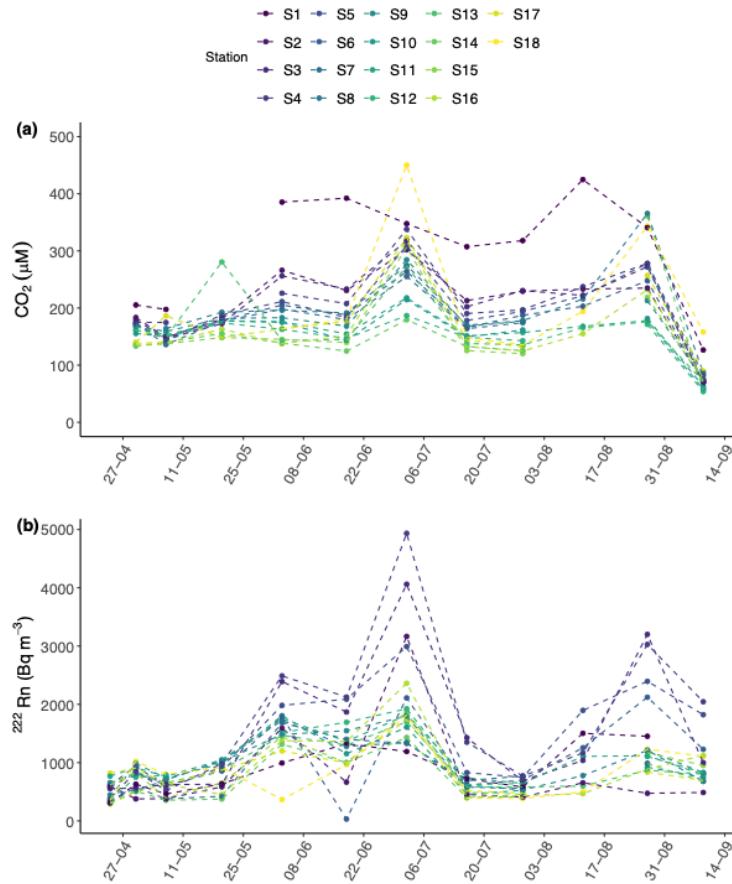


Figure 3: Temporal variation of (a) CO₂ and (b) ²²²Rn concentration in the stream during the study period (dates shown as DD-MM). Different colors represent different stations.

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

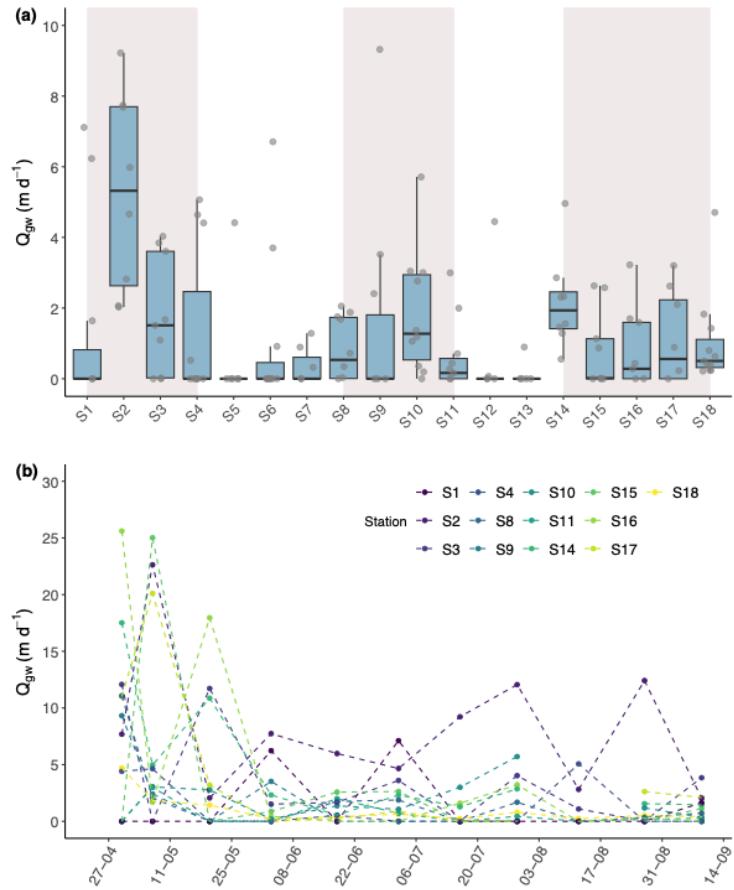


Figure 4: (a) Groundwater inflow rates along the stream reach. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile. The solid line inside the box indicates the median value. Whiskers extend to the most extreme data points within 1.5 times the IQR of the upper 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 $\text{g C m}^{-2} \text{ d}^{-1}$ (3.0 $\text{g C m}^{-2} \text{ d}^{-1}$, IQR: 1.9 – 4.9 $\text{g C m}^{-2} \text{ d}^{-1}$) across all stations and
 410 throughout the study period. The highest CO₂ emissions were found at the topmost station (S1),
 411 with 18.6 $\text{g C m}^{-2} \text{ d}^{-1}$ (IQR: 17.9 – 21.9 $\text{g C m}^{-2} \text{ d}^{-1}$). 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: $3.7 - 8.8 \text{ g C m}^{-2} \text{ d}^{-1}$), respectively. A gradual decline in CO_2 emissions was observed from S2 to S10, followed by a subsequent increase in CO_2 emissions from S11 to S16. Further downstream of station S16, CO_2 emissions decreased again, reaching $2.2 \text{ g C m}^{-2} \text{ d}^{-1}$ (IQR: $2.1 - 2.6 \text{ g C m}^{-2} \text{ d}^{-1}$) at the most downstream station (S18).

417

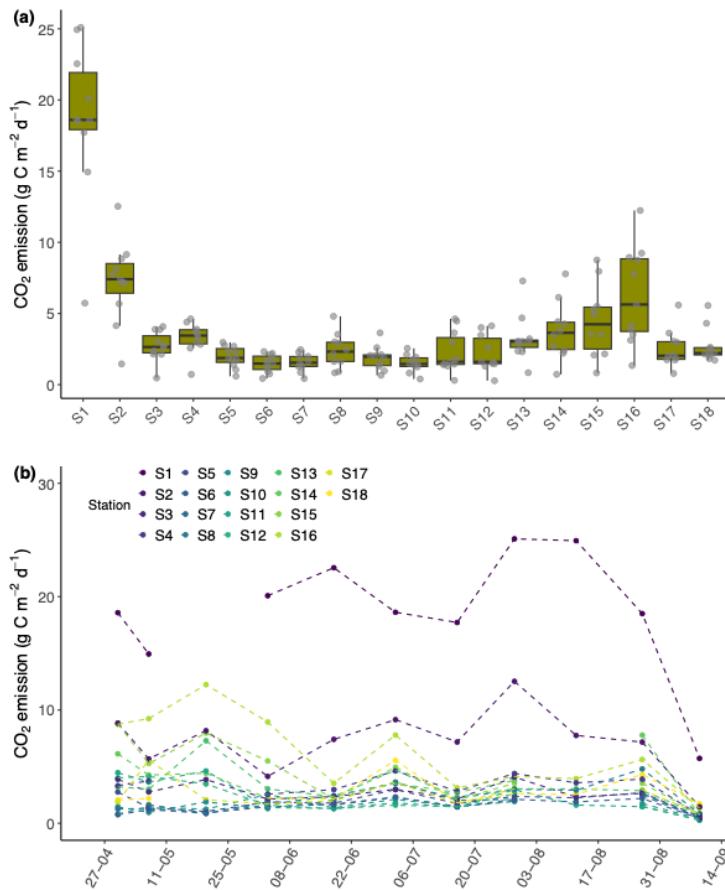


Figure 5: (a) Atmospheric emissions of CO_2 along the stream reach. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile, with the solid line inside the box indicating the median value. Whiskers extend to the most extreme data points within 1.5 times the IQR 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.

418



419 CO₂ emissions were relatively stable throughout the sampling period, with consistently
420 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.
421 5b). Afterwards, a notable decline in CO₂ emissions was observed, with a tendency of values in
422 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.

423 Downstream CO₂ export ranged from 9.2 to 864 g C m⁻² d⁻¹ (Fig. 6a). The median value
424 for all stream segments was similar ($F = 0.03, p = 1$), at 76 g C m⁻² d⁻¹. Downstream CO₂ export
425 fluctuated throughout the sampling season (Fig. 6b). During base-flow conditions between mid-
426 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
427 m⁻² d⁻¹). The highest amounts of CO₂ were exported downstream in early May, with a median value
428 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
429 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).

430 3.3.3. *Groundwater CO₂ inputs to the stream*

431 For stream segments with significant groundwater inflows, the CO₂ input via groundwater
432 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,
433 IQR: 0.00 – 50 g C m⁻² d⁻¹) exceeded the median atmospheric CO₂ emissions from these stream
434 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
435 CO₂ inputs were of the same order of magnitude as the CO₂ exported downstream (76 g C m⁻² d⁻¹,
436 IQR: 46 – 300 g C m⁻² d⁻¹). This suggests that a substantial proportion of the CO₂ delivered by
437 groundwater is transported downstream rather than being emitted into the atmosphere.

438 Groundwater CO₂ inputs showed strong temporal variability (Fig. S5). The highest CO₂
439 inflows were observed at the end of April, reaching a median value of 108 g C m⁻² d⁻¹ (IQR: 58 –
440 126 g C m⁻² d⁻¹). Inputs decreased towards the beginning of summer, but increased again in late
441 July, reaching a median value of 136 g C m⁻² d⁻¹ (IQR: 46 – 175 g C m⁻² d⁻¹). During baseflow
442 conditions, groundwater CO₂ inputs were consistently low, with median values of 10 g C m⁻² d⁻¹
443 (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.

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

450

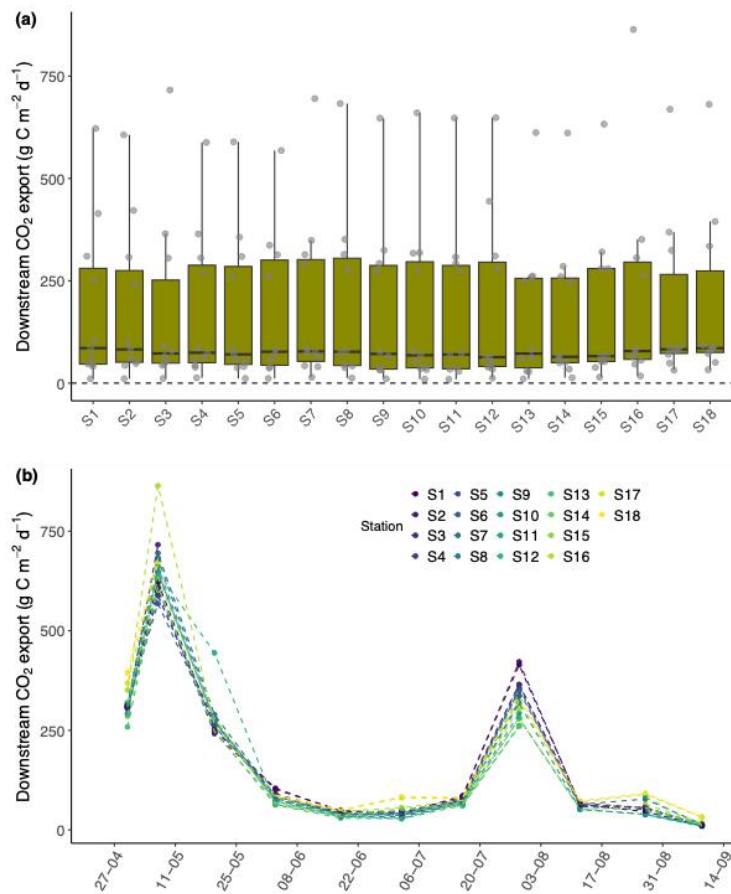


Figure 6: (a) Downstream CO_2 export across stream segments. Each box represents the interquartile range (IQR), spanning from the 25th to the 75th percentile, with the solid line inside the box indicating the median value. Whiskers extend to the most extreme data points within 1.5 times the IQR from the upper and lower quartiles. All individual observations used to construct the boxplots are plotted as grey circles. (b) Stream CO_2 export through the sampling season.

451

452

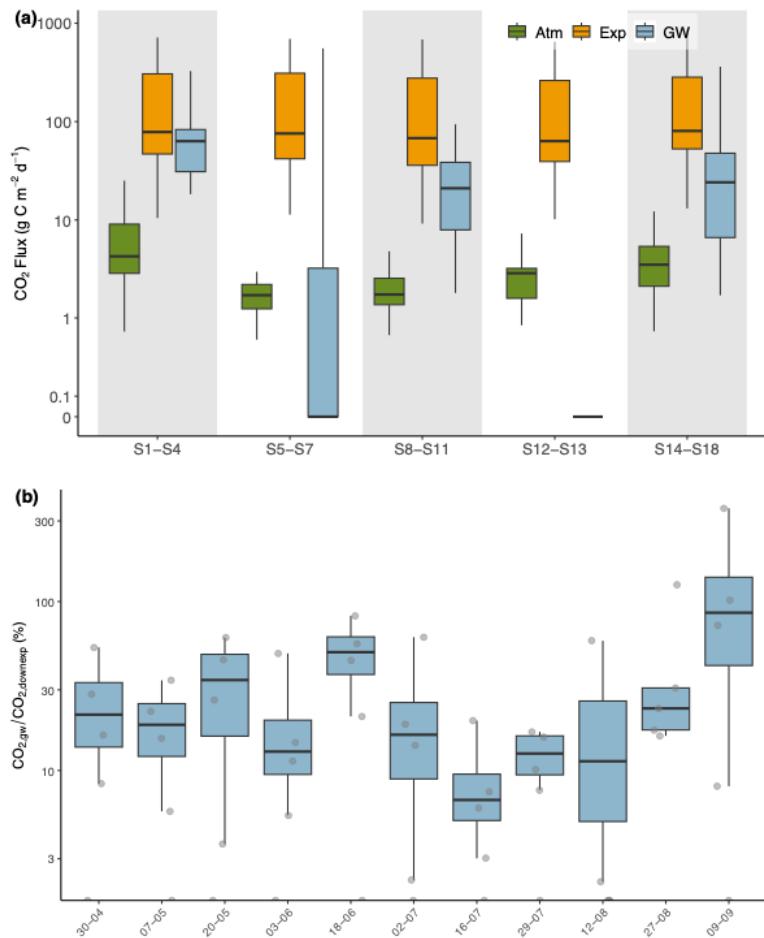


Figure 7. CO₂ fluxes in stream segments shown on a logarithmic scale. (a) Comparison of CO₂ fluxes via groundwater, atmospheric emissions, and downstream export. (b) Temporal variation in the relative contribution of groundwater CO₂ inputs to downstream CO₂ export along the stream. Each box represents 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**



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

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

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



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

500 **4.1.2 Temporal variations in groundwater CO₂ inputs**

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

515 CO₂ inputs via groundwater were also relatively high in late summer and early autumn (Fig.
516 S5), which coincided with precipitation events and associated increased stream discharge (see Fig.
517 S1). This pattern is consistent with previous observations showing that intensive rainfall events
518 recharge the groundwater system and enhance interactions between groundwater and surface
519 water, likely through rapid infiltration and increased hydraulic connectivity between the aquifer
520 and the stream. Groundwater recharge raises the water table (see Fig. S1b), thereby increasing the
521 hydraulic head gradient between the groundwater and the stream. This, in turn, drives higher
522 groundwater inflow rates (Cartwright & Gilfedder 2015) and reinforces the strong hydrological
523 coupling between surface water and groundwater in the study area. Additionally, higher soil
524 temperatures in summer compared to spring (Klaus et al., 2024) may accelerate the decomposition
525 of soil organic matter, thereby increasing the production of dissolved OC (DOC) in soil porewater
526 (Schelker et al., 2013). Root respiration during periods of peak primary production also contributes
527 to elevated CO₂ concentrations in soil and groundwater (Högberg et al., 2001). Together, these
528 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**



596 We acknowledge the assistance in the field and laboratory from Erik Geibrink and Anders Jonsson
597 at Umeå University. We also thank Morgan Karlsson, Christer Moreira Boman, and Hassan Ridha
598 for their assistance with installing the groundwater well and soil gas probe infrastructure, and
599 Valenti Rodellas for his help with ^{222}Rn analyses and his valuable comments and constructive
600 feedback. We acknowledge the Krycklan Catchment Study and the Swedish Infrastructure for
601 Ecosystem Science (SITES) for access to the sites and precipitation data, and the Biogeochemical
602 Analytical Facility (BAF) at Umeå University for chemical analysis.

603 **10 Financial support**

604 This study was financially supported by FORMAS (Grants no. 2018-01217 and 2018-00885) with
605 a grant awarded to CO and JK, and Stiftelsen Skogssällskapet (grant number 2019-657-Steg 2
606 2018) and The Geological Survey of Sweden (grant number 36-2788/2021) with grants awarded
607 to MK. CO acknowledges financial support from the Spanish Ministry of Science, Innovation and
608 Universities through the PERMAFLOW project (PID2023-148093NB-I00).

609 **11 References**

610 Adyasari, D., Dimova, N. T., Dulai, H., Gilfedder, B. S., Cartwright, I., McKenzie, T., and Fuleky,
611 P.: Radon-222 as a groundwater discharge tracer to surface waters, *Earth Sci. Rev.*, 238, 104321,
612 <https://doi.org/10.1016/j.earscirev.2023.104321>, 2023.

613 Ågren, A., Berggren, M., Laudon, H., and Jansson, M.: Terrestrial export of highly bioavailable
614 carbon from small boreal catchments in spring floods, *Freshwater Biol.*, 53, 964–972,
615 <https://doi.org/10.1111/j.1365-2427.2008.01955.x>, 2008.

616 Avery, E., Bibby, R., Visser, A., Esser, B., and Moran, J.: Quantification of Groundwater
617 Discharge in a Subalpine Stream Using Radon-222, *Water*, 10, 100,
618 <https://doi.org/10.3390/w10020100>, 2018.

619 Balathandayuthabani, S., Panneer Selvam, B., Gålfalk, M., Saetre, P., Peura, S., Kautsky, U.,
620 Klemetsson, L., Arunachalam, L., Vellingiri, G., Bastviken, D.: Methane in Two Stream
621 Networks: Similar Contributions From Groundwater and Local Sediments While Oxidation Was
622 a Large Sink Controlling Atmospheric Emissions, *J. Geophys. Res.: Biogeosci.*, 129,
623 e2023JG007836, <https://doi.org/10.1029/2023JG007836>, 2024.

624 Baxter, C., Hauer, F. R., and Woessner, W. W.: Measuring Groundwater–Stream Water Exchange:
625 New Techniques for Installing Minipiezometers and Estimating Hydraulic Conductivity, *Trans.*
626 *Am. Fish. Soc.*, 132, 493–502, [https://doi.org/10.1577/1548-8659\(2003\)132<0493:MGWENT>2.0.CO;2](https://doi.org/10.1577/1548-8659(2003)132<0493:MGWENT>2.0.CO;2), 2003.



628 Biehler, A., Buffin-Bélanger, T., Baudron, P., and Chaillou, G.: Groundwater discharge
629 contribution to dissolved inorganic carbon and riverine carbon emissions in a subarctic region.
630 *Biogeochemistry*, 165, 129–150, <https://doi.org/10.1007/s10533-023-01060-9>, 2023.

631 Blake, G., and Hartge, H.: Bulk density, In *Methods of Soil Analysis, Part 1 - Physical and*
632 *Minerological Methods* (2nd edition) (pp. 363–382), American Society of Agronomy - Soil
633 Science Society of America, Madison, 1986.

634 Boyle, D. R.: Design of a seepage meter for measuring groundwater fluxes in the nonlittoral zones
635 of lakes-Evaluation in a boreal forest lake. *Limnol. Oceanogr.*, 39, 670–681,
636 <https://doi.org/10.4319/lo.1994.39.3.0670>, 1994.

637 Briggs, M. A., Lautz, L. K., and McKenzie, J. M.: A comparison of fibre-optic distributed
638 temperature sensing to traditional methods of evaluating groundwater inflow to streams, *Hydrolog. Processes*, 26, 1277–1290, <https://doi.org/10.1002/hyp.8200>, 2012.

640 Burnett, W. C., Lambert, M., and Dulaiova, H.: Tracing groundwater discharge into the ocean via
641 continuous radon-222 measurements. *MTS/IEEE Oceans 2001. An Ocean Odyssey. Conference*
642 *Proceedings* (IEEE Cat. No.01CH37295), Honolulu, HI, USA, 2001, pp. 251-255 vol.1, <https://doi.org/10.1109/OCEANS.2001.968734>, 2001.

644 Cable, J. E., and Martin, J. B.: In situ evaluation of nearshore marine and fresh pore water transport
645 into Flamengo Bay, Brazil, *Estuarine Coastal Shelf Sci.*, 76, 473–483,
646 <https://doi.org/10.1016/J.ECSS.2007.07.045>, 2008.

647 Call, M., Sanders, C. J., Enrich-Prast, A., Sanders, L., Marotta, H., Santos, I. R., and Maher, D. T.:
648 Radon-traced pore-water as a potential source of CO₂ and CH₄ to receding black and clear water
649 environments in the Amazon Basin, *Limnol. Oceanogr. Lett.*, 3, 375–383,
650 <https://doi.org/10.1002/lol2.10089>, 2018.

651 Campeau, A., Bishop, K., Amvrosiadi, N., Billett, M. F., Garnett, M. H., Laudon, H., Öquist, M.G.,
652 Wallin, M.B.: Current forest carbon fixation fuels stream CO₂ emissions, *Nat. Commun.*, 10, 1876,
653 <https://doi.org/10.1038/s41467-019-09922-3>, 2019.

654 Campeau, Audrey, Lapierre, J. F., Vachon, D., and Del Giorgio, P. A.: Regional contribution of
655 CO₂ and CH₄ fluxes from the fluvial network in a lowland boreal landscape of Québec, *Global*
656 *Biogeochem. Cycles*, 28, 57–69, <https://doi.org/10.1002/2013GB004685>, 2014.

657 Cartwright, I., and Gilfedder, B.: Mapping and quantifying groundwater inflows to Deep Creek
658 (Maribyrnong catchment, SE Australia) using 222Rn, implications for protecting groundwater-
659 dependant ecosystems, *Appl. Geochem.*, 52, 118–129,
660 <https://doi.org/10.1016/j.apgeochem.2014.11.020>, 2015.



661 Chanyotha, S., Kranrod, C., abd Burnett, W. C.: Assessing diffusive fluxes and pore water radon
662 activities via a single automated experiment, *J. Radioanal. Nucl. Chem.*, 301, 581–588,
663 <https://doi.org/10.1007/s10967-014-3157-3>, 2014.

664 Cook, P. G.: Quantifying river gain and loss at regional scales, *J. Hydrol.*, 531, 749–758.
665 <https://doi.org/10.1016/j.jhydrol.2015.10.052>, 2015.

666 Corbett, D. R., Burnett, W. C., Cable, P. H., and Clark, S. B.: A multiple approach to the
667 determination of radon fluxes from sediments, *J. Radioanal. Nucl. Chem.*, 236, 247–253,
668 <https://doi.org/10.1007/BF02386351>, 1998.

669 Drake, T. W., Raymond, P. A., and Spencer, R. G. M.: Terrestrial carbon inputs to inland waters:
670 A current synthesis of estimates and uncertainty, *Limnol. Oceanogr. Lett.*, 3, 132–142.
671 <https://doi.org/10.1002/lo2.10055>, 2018.

672 Dyson, K. E., Billett, M. F., Dinsmore, K. J., Harvey, F., Thomson, A. M., Piirainen, S., and
673 Kortelainen, P.: Release of aquatic carbon from two peatland catchments in E. Finland during the
674 spring snowmelt period, *Biogeochemistry*, 103, 125–142, <https://doi.org/10.1007/s10533-010-9452-3>, 2011.

676 Hauptmann, D., Klaus, M., Sponseller, R. A., Olid, C., Laudon, J., and Karlsson, J. Discharge
677 modulates the dominance of downstream carbon export over evasion in a boreal headwater stream.
678 In Revision.

679 Högberg, P., Nordgren, A., Buchmann, N., Taylor, A. F. S., Ekblad, A., Högberg, M. N., Nyberg,
680 G., Ottosson-Löfvenius, M., and Read, D.D.: Large-scale forest girdling shows that current
681 photosynthesis drives soil respiration, *Nature*, 411, 789–792, <https://doi.org/10.1038/35081058>,
682 2001.

683 Hope, D., Palmer, S. M., Billett, M. F., and Dawson, J. J. C.: Variations in dissolved CO₂ and CH₄
684 in a first-order stream and catchment: an investigation of soil–stream linkages, *Hydrol. Processes*,
685 18(17), 3255–3275, <https://doi.org/10.1002/hyp.5657>, 2004.

686 Hotchkiss, E. R., Hall Jr, R. O., Sponseller, R. A., Butman, D., Klaminder, J., Laudon, H., Rosvall,
687 M., Karlsson, J.: Sources of and processes controlling CO₂ emissions change with the size of
688 streams and rivers. *Nat. Geosci.*, 8, 696–699, <https://doi.org/10.1038/ngeo2507>, 2015.

689 Klaus, M., Geibrink, E., Hotchkiss, E. R., and Karlsson, J.: Listening to air-water gas exchange in
690 running waters, *Limnol. Oceanogr-Meth.*, 17, 395–414, <https://doi.org/10.1002/lom3.10321>, 2019.

691 Klaus, M., Labasque, T., Botter, G., Durighetto, N., and Schelker, J.: Unraveling the Contribution
692 of Turbulence and Bubbles to Air-Water Gas Exchange in Running Waters, *J. Geophys. Res.-*
693 *Biogeosci.*, 127, e2021JG006520, <https://doi.org/10.1029/2021JG006520>, 2022.



694 Klaus, Marcus, Geibrink, E., Jonsson, A., Bergström, A.-K., Bastviken, D., Laudon, H.,
695 Klaminder, J., Karlsson, J.: Greenhouse gas emissions from boreal inland waters unchanged after
696 forest harvesting, *Biogeosciences*, 15, 5575–5594. <https://doi.org/10.5194/bg-15-5575-2018>,
697 2018.

698 Klaus, Marcus, Öquist, M., and Macháčová, K.: Tree stem-atmosphere greenhouse gas fluxes in a
699 boreal riparian forest. *Sci. Total Environ.*, 954, 176243.
700 <https://doi.org/10.1016/j.scitotenv.2024.176243>, 2024.

701 Kuglerová, L., Nilsson, G., and Hasselquist, E. M.: Too much, too soon? Two Swedish case studies
702 of short-term deadwood recruitment in riparian buffers, *Ambio*, 52, 440–452,
703 <https://doi.org/10.1007/s13280>, 2023.

704 Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, and Bishop, K. The Krycklan
705 catchment study - A flagship infrastructure for hydrology, biogeochemistry, and climate research
706 in the boreal landscape, *Water Resour. Res.*, 49, 7154–7158. <https://doi.org/10.1002/wrcr.20520>,
707 2013.

708 Laudon, H., Maher Hasselquist, E., Peichl, M., Lindgren, K., Sponseller, R., Lidman, F.,
709 Kuglerová, L., Hasselquist, N.J., Bishop, K., Nilsson, M.B., Ågren, A. M.: Northern landscapes in
710 transition: Evidence, approach and ways forward using the Krycklan Catchment Study, *Hydrol.
711 Processes*, 35, e14170, <https://doi.org/10.1002/hyp.14170>, 2020.

712 Laudon, H. and Ottosson Löfvenius, M.: Adding snow to the picture – providing complementary
713 winter precipitation data to the Krycklan Catchment Study database, *Hydrol. Processes*, 30, 2413–
714 2416, <https://doi.org/10.1002/hyp.10753>, 2016.

715 Laudon, H., Hasselquist, E. M., Peichl, M., Lindgren, K., Sponseller, R., Lidman, F., Kuglerová,
716 L., Hasselquist, N.J., Bishop, K., Nilsson, M.B., Ågren, A.M.: Northern landscapes in transition:
717 Evidence, approach and ways forward using the Krycklan Catchment Study. *Hydrological
718 Processes*, 35(4). <https://doi.org/10.1002/hyp.14170>, 2021.

719 Leach, J. A., Lidberg, W., Kuglerová, L., Peralta-Tapia, A., Ågren, A. M., and Laudon, H.:
720 Evaluating topography-based predictions of shallow lateral groundwater discharge zones for a
721 boreal lake-stream system, *Water Resour. Res.*, 53, 5420–5437, <https://doi.org/10.1002/>, 2017.

722 Ledesma, J. L. J., Futter, M. N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R. A., Laudon,
723 H., Bishop, K.J., and Köhler, J.: Towards an Improved Conceptualization of Riparian Zones in
724 Boreal Forest Headwaters, *Ecosystems*, 21, 297–315, <https://doi.org/10.1007/s10021-017-0149-5>,
725 2018.

726 Leith, F. I., Dinsmore, K. J., Wallin, M. B., Billett, M. F., Heal, K. V., Laudon, H., Öquist, M.G.,
727 Bishop, K.: Carbon dioxide transport across the hillslope–riparian–stream continuum in a boreal



728 headwater catchment, Biogeosciences, 12, 1881–1892, <https://doi.org/10.5194/bg-12-1881-2015>,
729 2015.

730 Li, M., Peng, C., Zhang, K., Xu, L., Wang, J., Yang, Y., Li, P., Liu, Z., and He N.: Headwater
731 stream ecosystem: an important source of greenhouse gases to the atmosphere, Water Res., 190,
732 116738, <https://doi.org/10.1016/j.watres.2020.116738>, 2021.

733 Libelo, E. L., and MacIntyre, W. G.: Effects Of Surface-Water Movement On Seepage-Meter
734 Measurements Of Flow Through The Sediment-Water Interface, Hydrogeol. J., 2, 49–54.
735 <https://doi.org/10.1007/s100400050047>, 1994.

736 Lupon, A., Denfeld, B. A., Laudon, H., Leach, J., Karlsson, J., and Sponseller, R. A.: Groundwater
737 inflows control patterns and sources of greenhouse gas emissions from streams, Limnol.
738 Oceanogr., 64, 1545–1557, <https://doi.org/10.1002/limo.11134>, 2019.

739 Lantmäteriet. GSD-Vegetationsdata (GSD vegetationdata, 2012).

740 Macintyre, S., Wanninkhof, R., and Chanton, J. P. Trace gas exchange across the air-water
741 interface in freshwater and coastal environments. In Biogenic Trace Gases: Measuring emissions
742 from soil and water (pp. 52–57.), 1995.

743 Maher Hasselquist, E., Lidberg, W., Sponseller, R. A., Ågren, A., and Laudon, H.: Identifying and
744 assessing the potential hydrological function of past artificial forest drainage, Ambio, 47, 546–
745 556, <https://doi.org/10.1007/s13280-017-0984-9>, 2017.

746 McGlynn, B. L., and McDonnell, J. J.: Quantifying the relative contributions of riparian and
747 hillslope zones to catchment runoff, Water Resour. Res., 39, 1310,
748 <https://doi.org/10.1029/2003WR002091>, 2003.

749 Mwakanyamale, K., Slater, L., Day-Lewis, F., Elwaseif, M., and Johnson, C.: Spatially variable
750 stage-driven groundwater-surface water interaction inferred from time-frequency analysis of
751 distributed temperature sensing data, Geophys. Res. Lett., 39, L06401,
752 <https://doi.org/10.1029/2011GL050824>, 2012.

753 Natchimuthu, S., Wallin, M. B., Klemedtsson, L., and Bastviken, D.: Spatio-temporal patterns of
754 stream methane and carbon dioxide emissions in a hemiboreal catchment in Southwest Sweden.
755 Sci. Rep., 7, 39729, <https://doi.org/10.1038/srep39729>, 2017.

756 Norstedt, G., and Laudon, H.: Krycklan: Markanvändning från forntid till nutid (in Swedish).
757 Retrieved from <https://pub.epsilon.slu.se/18715>, 2019.

758 Olid, C., Rodellas, V., Rocher-Ros, G., Garcia-Orellana, J., Diego-Feliu, M., Alorda-Kleinglass,
759 A., Bastviken, D., and Karlsson, J.: Groundwater discharge as a driver of methane emissions from
760 Arctic lakes, Nat. Comm., 13, 3667, <https://doi.org/10.1038/s41467-022-31219-1>, 2022.



761 Olid, C., Karlsson, J., Klaus, M., Hauptmann, D.
762 GWinputs_Emissions_Export_of_CO2_in_a_boreal_stream.figshare.
763 <https://doi.org/10.6084/m9.figshare.30501437.vs>, 2025.

764 Öquist, M. G., Wallin, M., Seibert, J., Bishop, K., and Laudon, H.: Dissolved inorganic carbon
765 export across the soil/stream interface and its fate in a boreal headwater stream. *Environ. Sci.*
766 *Technol.*, 43, 7364–7369. <https://doi.org/10.1021/es900416h>, 2009.

767 Rasilo, T., Hutchins, R. H. S., Ruiz-González, C., and del Giorgio, P. A.: Transport and
768 transformation of soil-derived CO₂, CH₄ and DOC sustain CO₂ supersaturation in small boreal
769 streams, *Sci. Total Environ.*, 579, 902–912, <https://doi.org/10.1016/j.scitotenv.2016.10.187>, 2017.

770 Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D.,
771 Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., and Guth,
772 P.: Global carbon dioxide emissions from inland waters, *Nature*, 503, 355–9,
773 <https://doi.org/10.1038/nature12760>, 2013.

774 R Core Team: R: A language and environment for statistical computing. R Foundation for
775 Statistical Computing. Retrieved from <http://www.R-project.org/>, 2017.

776 Rosenberry, D. O.: A seepage meter designed for use in flowing water. *J. Hydrol.*, 359, 118–130,
777 <https://doi.org/10.1016/j.jhydrol.2008.06.029>, 2008.

778 Schelker, J., Grabs, T., Bishop, K., and Laudon, H.: Drivers of increased organic carbon
779 concentrations in stream water following forest disturbance: Separating effects of changes in flow
780 pathways and soil warming, *J. Geophys. Res. Biogeosci.* 118, 1814–1827,
781 <https://doi.org/10.1002/2013JG002309>, 2013.

782 Schmadel, N. M., Neilson, B. T., and Stevens, D. K.: Approaches to estimate uncertainty in
783 longitudinal channel water balances, *J. Hydrol.*, 394, 357–369,
784 <https://doi.org/10.1016/j.jhydrol.2010.09.011>, 2010.

785 Schubert, M., Paschke, A., Lieberman, E., & Burnett, W. C.: Air-water partitioning of 222Rn and
786 its dependence on water temperature and salinity, *Environ. Sci. Technol.*, 46, 3905–3911.
787 <https://doi.org/10.1021/s204680n>, 2012.

788 Stanley, E. H., Loken, L. C., Casson, N. J., Oliver, S. K., Sponseller, R. A., Wallin, M. B., Zhang,
789 L., and Rocher-Ros, G.: GRiMeDB: the Global River Methane Database of concentrations and
790 fluxes, *Earth Syst. Sci. Data*, 15, 2879–2926, <https://doi.org/10.5194/essd-15-2879-2023>, 2023.

791 Stieglitz, T. C., Beek, P., Souhaut, M., and Cook, P. G.: Karstic groundwater discharge and
792 seawater recirculation through sediments in shallow coastal Mediterranean lagoons, determined



793 from water, salt and radon budgets, Mar. Chem., 156, 73–84,
794 <https://doi.org/10.1016/j.marchem.2013.05.005>, 2013.

795 Stumm, W., and Morgan, J. J.: Aquatic Chemistry: Chemical Equilibria and Rates in Natural
796 Waters (Vol. 10: 0471511854). ISBN 0471511854, 9780471511854.: Wiley., 1995.

797 Venkiteswaran, J. J., Schiff, S. L., and Wallin, M. B.: Large Carbon Dioxide Fluxes from
798 Headwater Boreal and Sub-Boreal Streams, PLoS One, 9, e101756,
799 <https://doi.org/10.1371/journal.pone.0101756>, 2014.

800 Wallin, M. B., Campeau, A., Audet, J., Bastviken, D., Bishop, K., Kokic, J., Laudon, H., Lundin,
801 E., Löfgren, S., Natchumuthu, S., Sobek, S., Teutschbein, C., Weyhenmeyer, G.A., Grabs, T.:
802 Carbon dioxide and methane emissions of Swedish low-order streams—a national estimate and
803 lessons learnt from more than a decade of observations, Limnol. Oceanogr. Lett., 3, 156–167,
804 <https://doi.org/10.1002/lol2.10061>, 2018.

805 Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean revisited,
806 Limnol. Oceanogr. Methods, 12, 351–362, <https://doi.org/10.4319/lom.2014.12.351>, 2014.

807 Westhoff, M. C., Bogaard, T. A., and Savenije, H. H. G.: Quantifying spatial and temporal
808 discharge dynamics of an event in a first-order stream, using distributed temperature sensing,
809 Hydrol. Earth. Syst. Sci., 15, 1945–1957. <https://doi.org/10.5194/hess-15-1945-2011>, 2011.

810

811