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Key Points:

- We identified a geomorphological “control point” to deliver respiratory CO₂ from soils to an Alpine stream via groundwater
- We show how streamwater CO₂ dynamics and evasion varies with stream network expansion and contraction
- CO₂ evasion from mountain streams might be underestimated due to high spatiotemporal variability in pCO₂

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High-Resolution Spatial Sampling Identifies Groundwater as Driver of CO₂ Dynamics in an Alpine Stream Network

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Abstract Inland waters are major sources of CO₂ to the atmosphere. The origin of this CO₂ is often elusive, especially in high-altitude streams that remain poorly studied at present. Here we study the spatial and seasonal variations in streamwater CO₂, its potential sources and drivers in an Alpine stream network (Switzerland). High-resolution sampling combined with stable isotope analysis and mixing models enabled us to capture the fine-scale spatial heterogeneity in streamwater pCO₂ as the stream network expanded and contracted during seasons. We identified soil respiration as a major source of CO₂ to the stream. We also identified a major groundwater upwelling zone as an ecosystem “control point” that disproportionately influenced stream biogeochemistry. This was particularly pronounced when the stream network expanded during snowmelt, when it covered a five times larger area compared to winter (35,300 m² compared to 7,100 m²). Downstream from this control point, CO₂ evaded rapidly owing to high gas transfer velocity. The stream network was a net source of CO₂ to the atmosphere with an average areal evasion flux of 30.1 (18.0–43.1) μmol · m⁻² · s⁻¹ and a total flux at network scale ranging from 237 (141–339) kg C/day in winter to 1793 (1069–2565) kg C/day during spring snowmelt. Our study highlights the role of stream network dynamics and control points for the CO₂ dynamics in high-altitude streams.

Plain Language Summary Streams are significant sources of CO₂ to the atmosphere. However, the origin of this CO₂ and its spatial and temporal dynamics are often not clear. Here we study the small-scale spatial variation of streamwater CO₂ and its evasion from an Alpine stream network in Switzerland. We found that groundwater upwelling, as constrained by local geomorphology, delivered large quantities of respiratory CO₂ from adjacent soils to the stream. The relevance of these groundwater deliveries changes seasonally as the stream network expanded and contracted. Our spatially resolved sampling design allowed us to identify hot spots of CO₂ evasion, based on which we were able to assess CO₂ evasion at the scale of the entire stream network. Our findings emphasize the relevance of such approaches to properly constrain CO₂ evasion fluxes beyond the reach scale.

1. Introduction

Inland waters are key components of the global carbon cycle. They transport and store organic and inorganic carbon but also transform carbon with the ultimate emission of carbon dioxide (CO₂) and methane (CH₄) to the atmosphere (Battin et al., 2009; Cole et al., 2007; Raymond et al., 2013; Stanley et al., 2016). While high-latitude streams are recognized as large emitters of CO₂ (e.g., Campeau et al., 2014; Öquist et al., 2009; Wallin et al., 2011), the emissions of CO₂ from high-altitude streams are less well studied at present (Crawford et al., 2013; Lauerwald et al., 2015; Schelker et al., 2016). This is remarkable given the susceptibility of high-altitude streams to climate change, where glacier retreat and shifts in precipitation patterns, with consequences for snowpack distribution, change the hydrological and thermal regimes (Barnett et al., 2005; Milner et al., 2017) and carbon fluxes (Ulseth et al., 2018).

While a third of the CO₂ evasion from streams and rivers occurs in headwater catchments (Marx et al., 2017), it is only recently that attempts are being made to constrain the sources of the CO₂ in these streams (e.g., Duvert et al., 2018; Hotchkiss et al., 2015). Overall, these studies suggest that terrestrial deliveries of CO₂ prevail in headwaters and that autochthonous CO₂ sources (e.g., from aquatic ecosystem respiration) become more important downstream. This is, among other reasons, because of the typically high hydrological connectivity between groundwater with their adjacent soils in headwater streams (Butman &

Ulseth, Torsten W. Vennemann, Tom J. Battin

Raymond, 2011; Crawford et al., 2013; Peter et al., 2014). Shallow groundwater transports CO₂ derived from soil respiration (e.g., Campeau et al., 2018), while deeper groundwater can entrain dissolved inorganic carbon (DIC) from carbonaceous rock weathering (Amiotte Suchet et al., 2003) into the streams. The upwelling of groundwater may therefore locally enrich streamwater in CO₂ (and DIC) and subsequently increase CO₂ evasion fluxes along downstream reaches (Crawford et al., 2014; Duvert et al., 2018). Such zones of local groundwater upwelling may function as “control points” that spatially and temporally control ecosystem dynamics and related biogeochemical fluxes (in the sense of Bernhardt et al., 2017). If not properly accounted for, the rapid local CO₂ evasion downstream from such control points may lead to an underestimation of CO₂ evasion rates at larger scales (i.e., reach scale and beyond; Deirmendjian & Abril, 2018; Duvert et al., 2018). Thus, insights in catchment hydrology and streamwater sources are helpful for tracking the sources and fate of streamwater CO₂.

The sources of CO₂ in streamwater can be identified using stable carbon isotope analyses (Campeau et al., 2018; Kendall & Caldwell, 1998; Venkiteswaran et al., 2014). $\delta^{13}\text{C}$ values of streamwater CO₂ depend on the relative contribution of carbon from respiration, weathering, and atmospheric exchange (e.g., Finlay, 2001). Isotopic discrimination occurs during CO₂ assimilation by plants, where the lighter isotope is preferentially used over the heavier isotope. CO₂ originating from in-stream or soil respiration (either from root respiration or heterotrophic oxidation of soil organic matter) has $\delta^{13}\text{C}$ values similar to those of the organic carbon being respired (Doctor et al., 2008), commonly ranging between -34 and -24‰ (e.g., Wang et al., 2012) in temperate environments where C3 is the most abundant photosynthetic pathway (Still et al., 2003). In the presence of carbonate bedrock, calcium carbonate dissolution (with $\delta^{13}\text{C}$ values close to zero) commonly occurs due to a reaction with carbonic acid (H₂CO₃) originating from soil respiration (Clark & Fritz, 1997). Therefore, in streams with carbonate mineral dissolution, streamwater CO₂ is typically enriched in ¹³C with values ranging from -23 to -11‰ (Mayorga et al., 2005). Moreover, during exchange with atmospheric CO₂, the lighter ¹²C isotopes evade more easily from the streamwater, which results in an enrichment of streamwater CO₂ and DIC in the heavier isotope ¹³C (Polensaere & Abril, 2012; Venkiteswaran et al., 2014).

The aim of this study was, using high-resolution spatial surveys, to study the dynamics of CO₂, its sources, and evasion fluxes from an Alpine headwater stream network as it expands and contracts during seasons. Alpine catchments, with their hydrology being dominated by snow and glacier ice melt, are well suited to study the dynamics of hydrological connectivity and its impact on stream biogeochemistry. In fact, the hydrology of alpine streams is shaped by the relative contributions from groundwater, precipitation, snow-melt, and glacier ice melt, all of them changing seasonally and becoming increasingly altered because of global warming (Milner et al., 2017). We hypothesized that the spatial and temporal variability of groundwater upwelling is a major driver of the dynamics of streamwater pCO₂ and CO₂ evasion fluxes from the stream network. We also anticipated that local valley geomorphology can act as a control point (in the sense of Bernhardt et al., 2017) that, depending on the hydrology, modulates groundwater upwelling and hence CO₂ delivery into the stream. Furthermore, we expected the hydrological connectivity as modulated by seasonal expansion and contraction of the stream network, together with seasonal fluctuation of shallow groundwater dynamics, to influence pCO₂ dynamics and CO₂ evasion fluxes.

2. Materials and Methods

2.1. Study Site Description

We conducted field surveys in the stream network draining the Vallon de Nant catchment (13.4 km², 46°15′ 12.3″N, 7° 06′34.7″E) in the Swiss Alps (Figure 1). Catchment boundaries were delineated in ArcGIS 10.5 (Environmental Systems Research Institute, USA) using a digital elevation model (DEM; 2-m² resolution; Geodata © Swisstopo). The catchment elevation ranges from 1,190 to 3,051 m above sea level. The upstream catchment is characterized by a wide valley bottom with braided and low-sloped channels. Downstream from this braided area, the valley geomorphology constrains the stream into a canyon-like channel that gradually opens up again further downstream (Figure 1). The average catchment slope is 0.32 m/m, and the average stream channel slope is 0.093 ± 0.033 m/m. The stream network, with a maximum stream length of 4,500 m, expands and contracts throughout the year depending on the variable contributions from snow-melt, glacier ice melt, groundwater, and precipitation (Figure 2). The glacier, situated in the southeast part of

Figure 1. Topographic map of the study catchment, Vallon de Nant (Switzerland) with an elevation ranging from 1,190 to 3,051 m above sea level (asl). The geomorphological transition partitions the stream channels in an upstream braided system and a downstream canyon-like system. Shown are 10-m elevation contour lines extracted from a digital elevation model, derived in QGIS 3.2.1 (QGIS Development Team, Switzerland) Data source: Geodata © Swisstopo.

the catchment, covers 5% of the catchment area. Vegetation cover consists of natural grassland (18%), coniferous forest (15%), sparsely vegetated areas (13%), and moors and peatland (4%); roughly 45% of the catchment consists of bare rock, including calcareous minerals, estimated in ArcGIS from CORINE land cover (European Environment Agency, Denmark). In 2016, the annual air temperature averaged 5.9 ± 6.1 °C and streamwater temperature averaged 4.8 ± 2.8 °C.

2.2. Sampling Design

We conducted sampling campaigns (2016) in winter (March), spring (May), summer (September), and autumn (November) and timed them to capture the seasonal hydrological variability typical for Alpine catchments. During each season, streamwater samples were collected during 3 to 4 days along the main channel and intermittent tributaries approximately every 50 to 80 m, starting from the catchment outlet to a maximal length of 4,500 m upstream depending on the network expansion. Hereafter, we refer to the various sampling sites as the linear distance upstream from the catchment outlet (i.e., from the most downstream site in our sampling sequence). We systematically restricted the sampling window and only sampled between 6 a.m. and 12 a.m. in order to avoid effects from diurnal fluctuations in streamwater chemistry owing to glacier ice melt and snowmelt later during the day. Moreover, we compared the daily fluctuations in streamwater temperature in the catchment outlet (measured every 10 min) to the instantaneous values measured during sampling to verify that we sampled well within that window of relative stability. During sampling in winter, large parts of the stream network were snow-covered, which precluded sampling in the reaches beyond a distance of 2,700 m upstream from the outlet. During this time the stream network was at maximum contraction. During spring snowmelt, water flow in tributaries and locally emerging subsurface flow paths transiently expanded the network. In summer, glacier ice melt provided water flow to the stream reach directly downstream from the glacier, a channel which fell dry again in autumn. In autumn, various springs along the northwestern flank of the catchment contributed to stream flow in the main channel.

The network behavior allowed us to collect streamwater samples from a total of 43 sites in late winter (March), 118 sites in spring (May), 75 sites in summer (September), and 64 sites in autumn (November); sampling sites along the main stem slightly differed between seasons.

2.3. Chemical Composition of Streamwater

Streamwater was collected from the thalweg to analyze a suite of parameters. Samples were stored in the dark (4°C) pending analyses in the laboratory within 24 hr. We also measured streamwater pH, temperature, and specific conductivity (SC) in the field with daily calibrated WTW multiparameter probes (Xylem Inc., USA).

We collected water samples for CO₂ concentration and isotopic composition ($\delta^{13}\text{C-CO}_2$). Duplicate samples were collected in glass vials (60 ml) that contained crystallized sodium azide (300 μl) for sample preservation (Schelker et al., 2016). In the field, vials were carefully submerged in the water to avoid bubble formation and turbulence-induced CO₂ loss, and while still submerged, the vials were sealed with rubber stoppers and metal caps. Back in the lab, a headspace with synthetic air (<5 ppm CO₂) was created and the water phase and the headspace were equilibrated (2 hr; Schelker et al., 2016). We measured the CO₂ concentrations and isotopic compositions using a cavity ring-down spectrometer (G2201-I, Picarro Instruments, USA). In the beginning and end of each laboratory day, we analyzed blanks with synthetic air to ensure that it contained less than 5 ppm of CO₂. At each sampling site in the field, we also sampled air into glass vials (60 ml) for the determination of atmospheric CO₂ using the same cavity ring-down spectrometer as above.

Figure 2. Samples were taken every 50 m along the nivo-glacial headwater stream network, during winter, spring, summer, and autumn. The circles specify each sampling location during the four campaigns. The stream network expanded and contracted throughout the year. (a-d) A distinct increase in specific conductivity (maps) is noted approximately 2,800 m (± 100 m) upstream, in a braided stream segment. (e-h) This corresponds to an increase in discharge in the same stream segment.

For DIC concentrations and isotopic compositions ($\delta^{13}\text{C}$ -DIC), streamwater was filtered directly in the field (0.47- μm nylon filter) into 40-ml glass vials (one vial per site). We assessed the possibility of degassing CO_2 because of filtration; the risk of underestimation of DIC was found to be small since DIC mostly consisted of HCO_3^- ($97 \pm 0.6\%$) and the proportion of dissolved free CO_2 was $2.4 \pm 0.7\%$ due to elevated streamwater pH (8.14 ± 0.12). For the measurements of DIC in the laboratory, we added 200 μl of 85% orthophosphoric acid into empty glass vials, which we flushed with helium to avoid background CO_2 . We then injected 1.5 ml of streamwater and equilibrated the samples for 2 hr in the helium headspace. Next, we measured DIC as the CO_2 released by the reaction with the orthophosphoric acid using isotope ratio mass spectrometry (FinniganTM GasBench II, Thermo Finnigan DeltaPlus XL, USA; Spötl & Vennemann, 2003). The measured values were normalized with an in-house standard, Carrara Marble II, which was analyzed in the beginning and the end of each sequence as well as dispersed throughout the sequence between every 8 to 10 samples.

Streamwater samples were also analyzed for dissolved organic carbon (DOC), alkalinity, major anions and cations, and deuterium (δD) and oxygen ($\delta^{18}\text{O}$) stable isotopes. Samples for DOC analysis were filtered through double GF/F filters (Whatman) into 40-ml acid-washed and precombusted glass vials and analyzed within 1 to 3 days (Sievers M5310c TOC Analyzer, GE Analytical Instruments, USA). The accuracy of the instrument is $\pm 2\%$, precision $<1\%$, and detection limit 1.83 $\mu\text{mol C/L}$ (N. Escoffier, personal communication, 16 April 2018). Nonfiltered samples for the estimation of streamwater alkalinity were collected in 500-ml polyethylene bottles and analyzed by titration with 0.05 N HCl. For quality control, titrations were performed on freshly opened Evian[®] bottled water, which has a constant and known alkalinity. We

Table 1
End-Members for the Mixing Model

Parameters	Glacial stream	Groundwater	Nival stream
$\delta^{18}\text{O}$ (‰ VSMOW)	-12.8 (0.03)	-12.7 (N/A)	-14.6 (0.16)
Specific Conductivity ($\mu\text{S}/\text{cm}$)	165.6 (0.67)	272.0 (N/A)	138.1 (7.35)

Note. Glacial stream ($n = 12$), groundwater ($n = 1$), and nival stream ($n = 27$). Values are means (standard deviations). Abbreviation: N/A, not available.

performed the alkalinity measurements with both manual and automatic titration (916_Ti-touch automatic titrator, Metrohm, Switzerland). Concentrations of major anions and cations were measured on streamwater filtered through 0.22- μm filtered (Mixed Cellulose Ester) using ion chromatography (ICS-3000 Dionex, USA). Finally, values of streamwater δD and $\delta^{18}\text{O}$ were determined on filtered (0.47 μm) samples using a Picarro cavity ring-down spectrometer (L1102-i).

Discharge (Q) was estimated approximately every 300 m using slug additions of dissolved sodium chloride (NaCl) into the streamwater and measuring the changes of streamwater SC downstream. We established an empirical relationship between NaCl concentration and SC and calculated the discharge from the breakthrough curves (similar to Peter et al., 2014). We measured channel width at every sampling site to estimate the surface area of the stream network for each season. We also calculated streambed area between sites with Q measurements, from which we inferred areal specific stream discharge (Δq).

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2.4. Data Analysis

The relative contributions from groundwater, snowmelt, and glacier ice melt (Table 1) were estimated using a Bayesian end-member mixing model with the *R* package *simmr* (Parnell, 2016). A dual-tracer approach was used to achieve a two-dimensional plane of the potential water source contributions. Due to the similarity of the stable isotopic composition of groundwater and glacier ice melt, we performed mixing analyses using $\delta^{18}\text{O}$ as the first tracer and SC as the second tracer; these are common tracers for end-member mixing analyses (Barthold et al., 2011). The glacial stream end-member was sampled close to the glacier during summer ($n = 12$). Several nival tributaries were sampled during the spring campaign, across the stream network, and the $\delta^{18}\text{O}$ and SC of these sites served as the nival stream source ($n = 27$). The groundwater end-member values were obtained from a 5-m-deep groundwater well installed in a large alluvial aquifer system below the braided reach 2,800-m upstream. Groundwater is generally well mixed here and expected to be relatively stable in terms of its geochemistry (J. Thornton, personal communication, 4 April 2019). We received groundwater $\delta^{18}\text{O}$ data from this well in August 2017 and determined SC, $p\text{CO}_2$, DIC, and isotopic compositions of CO_2 and DIC in October 2017.

We used changepoint analysis (Killick & Eckley, 2014) with the *R* package *changepoint* (Killick et al., 2016) to detect shifts in streamwater constituents along the main channel.

Sources of CO_2 and DIC were explored using Keeling (Keeling, 1958) and Miller-Tans (Miller & Tans, 2003) linear mixing models. Both models are based on the assumption that the mixing of two different sources with different isotopic compositions create a two-dimensional space that can be described by a simple linear model ($y = ax + b$). The mass balances for CO_2 and $\delta^{13}\text{C}\text{-CO}_2$ (and correspondingly for DIC and $\delta^{13}\text{C}\text{-DIC}$) give the following relationship,

$$\delta^{13}\text{C}_M \times C_M = \delta^{13}\text{C}_S \times C_S + \delta^{13}\text{C}_B \times C_B \quad (1)$$

where the measured isotopic composition ($\delta^{13}\text{C}_M$) and concentration (C_M) equal the sum of the isotopic composition and concentration of the source ($\delta^{13}\text{C}_S$ and C_S) and the background ($\delta^{13}\text{C}_B$ and C_B). $\delta^{13}\text{C}_S$ and C_S represent the sum of all carbon sources, while $\delta^{13}\text{C}_B$ and C_B are the composition of atmospheric CO_2 (Campeau et al., 2017; Keeling, 1958; Miller & Tans, 2003). From equation (1), the equations for the Keeling, equation (2), and Miller-Tans, equation (3), plots are derived as

$$\delta^{13}\text{C}_M = C_B (\delta^{13}\text{C}_B \times \delta^{13}\text{C}_S) \times (1/C_M) + \delta^{13}\text{C}_S \quad (2)$$

$$\delta^{13}\text{C}_M \times C_M = \delta^{13}\text{C}_S \times C_M - C_B (\delta^{13}\text{C}_B - \delta^{13}\text{C}_S) \quad (3)$$

In the Keeling plot, the measured streamwater $\delta^{13}\text{C}$ is plotted against the inverse carbon concentration ($1/C$) where the y-intercept equals to the $\delta^{13}\text{C}$ of the source (Keeling, 1958; Pataki et al., 2003). In the Miller-Tans plot, the observed isotopic ratio is multiplied by the concentration and expressed as a function of the

measured concentration, where the slope represents the $\delta^{13}\text{C}_\text{S}$ value. Keeling and Miller-Tans models are based on linear mixing, and we acknowledge that isotopic fractionation (e.g., during CO_2 evasion) can violate that assumption. Therefore, additional to applying the Keeling and Miller-Tans models to the measured CO_2 and DIC concentrations and isotopic compositions, we also estimated CO_2 sources from theoretically calculated CO_2 concentrations (e.g., Weyhenmeyer et al., 2012) and theoretically calculated isotopic compositions (Campeau et al., 2017; Mook et al., 1974; Zhang et al., 1995; from DIC concentration, $\delta^{13}\text{C}$ -DIC and streamwater temperature) assuming an isotopic fractionation of $\delta^{13}\text{C}$ - CO_2 in equilibrium with DIC. Hence, we could better constrain the effect of CO_2 evasion for the estimation of CO_2 sources because rapid CO_2 evasion can drastically change its isotopic composition.

We estimated CO_2 evasion fluxes for winter, spring, summer, and autumn, using seasonal median $p\text{CO}_2$ values combined with the empirical k_{600} equation from Ulseth et al. (2019). Briefly, we derived k_{600} from seasonal average energy dissipation (eD , m^2/s^3), where eD is a product of flow velocity (V , m/s), channel slope (S , m/m), and the gravitational acceleration (m/s^2 ; equation (4)). To incorporate the large variation in stream channel slope along the stream network, and the potential impact slope might have on the resulting flux estimates, we used average stream channel slope ($\pm$ standard deviation) for the calculations. Since eD was higher than $0.02 \text{ m}^2/\text{s}^3$ we used the equation established for turbulent and high-energy streams.

$$k_{600} = \exp^{6.43+1.18 \times \ln(eD)} \quad (4)$$

k_{CO_2} was then estimated from k_{600} using the Schmidt number scaling (Sc_{CO_2} ; Wanninkhof, 1992), which is temperature ($T^\circ\text{C}$) dependent,

$$Sc_{\text{CO}_2} = 1911.1 - 118.11 \times T + 3.4527 \times T^2 - 0.041320 \times T^3 \quad (5)$$

$$k_{\text{CO}_2} = k_{600} \times \frac{Sc_{\text{CO}_2}}{600}^{-0.5} \quad (6)$$

where the exponent of -0.5 is commonly used for turbulent water (Jähne et al., 1987).

3. Results

3.1. Variation in Discharge

Discharge in the main channel of the stream network varied seasonally and spatially (Figure 2). Average discharge was lowest during winter baseflow (70 L/s), increased tenfold, and was highest in spring during snowmelt (970 L/s) to gradually decrease again during glacier ice melt in summer (230 L/s), and back to baseflow in autumn (140 L/s). Along the mainstem, discharge increased markedly around 2,800 m upstream where the braided channels transitioned into constrained canyon-like channel (Figure 1). Here the specific discharge was 1.30 , 0.25 , and $0.13 \text{ L} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ in spring, summer, and autumn, respectively; changes in specific discharge could not be estimated in winter because of snow cover. The spatial variation in discharge downstream of this gaining reach was generally low.

3.2. Spatial and Seasonal Variations in Source Contributions to Streamflow

Contributions from groundwater, glacial ice melt, and snowmelt to streamflow changed seasonally and were linked to the expansion and contraction dynamics of the stream network. The end-member mixing analysis showed that groundwater was the dominant source of water in winter, spring, and autumn (Figure 3). Groundwater was relatively stable downstream ($<2,800 \text{ m}$) from the braided reach, with contributions of 65.5 ± 2.8 , 61.8 ± 2.9 , 40.8 ± 1.5 , and $54.1 \pm 2.1\%$ in winter, spring, summer, and autumn, respectively. No mixing model estimates were computed for the upstream reaches ($>2,800 \text{ m}$) in winter because of the lack of data owing to the snow cover. In spring, however, groundwater contributions were lower in the upstream reaches ($34.2 \pm 12.2\%$) compared to downstream reaches, while snow melt contributed $58.1 \pm 10.8\%$ to the streamflow upstream. In summer, glacier ice melt was the primary source ($92.2 \pm 18.5\%$) to streamwater flow in reaches above 2,800 m. Owing to lateral groundwater upwelling, glacier ice melt contributed only $45.4 \pm 6.2\%$ to the streamflow in the downstream reaches. During autumn, groundwater contributed on average $45.9 \pm 23.9\%$ to the streamflow in the upstream reaches (2,800 m) and were relatively constant along the mainstem.

Figure 3. $\delta^{18}\text{O}$ values and specific conductivity of the streamwater sources and of the water collected along the stream network across the four seasonal sampling campaigns. The dashed line indicates the two-dimensional space between the three identified water source contributions as obtained from the Bayesian mixing model; (a) groundwater, glacial stream flow, and nival stream flow. Water source contribution and difference in specific stream discharge (q) varied across (b) winter, (c) spring, (d) summer, and (e) autumn. The difference in specific discharge (q) was highest in the braided stream reach, where groundwater contributions increased in spring and summer.

3.3. Spatial and Seasonal CO_2 Dynamics

Streamwater $p\text{CO}_2$ averaged $634 \pm 108 \mu\text{atm}$ during the study year and varied seasonally and spatially along the mainstem of the stream network (Figure 4 and Table 2). Streamwater was supersaturated in CO_2 with respect to the atmosphere for 92% of all sample sites across the stream network and over all four seasons ($n=247$). In the mainstem, streamwater CO_2 supersaturation was observed in 93% of the sampling sites ($n=159$). The maximum streamwater $p\text{CO}_2$ ($1,305 \mu\text{atm}$) was measured in a spring-fed stream draining into

Figure 4. Spatial variations in (a–d) $p\text{CO}_2$ and groundwater contributions and (e–h) measured and calculated $\delta^{13}\text{C-CO}_2$. The mainstem streamwater $p\text{CO}_2$ varied across winter (a), spring (b), summer (c), and autumn (d). The groundwater contributions increased in the braided stream segment during spring and summer (marked with a gray band) simultaneously as the isotopic compositions of CO_2 became more depleted in ^{13}C . The calculated isotopic compositions of CO_2 followed the same spatial dynamic patterns as the measured isotopic compositions of CO_2 .

Table 2*Dissolved Organic and Inorganic Carbon Concentrations, Isotopic Values of DIC, and CO₂, and pCO₂*

Season	Mainstem sampling sites	Mean pCO ₂ (μatm)	Mean DOC (mmol/L)	Mean DIC (mmol/L)	Mean δ ¹³ C-DIC (‰VPDB)	Mean δ ¹³ C-CO ₂ (‰VPDB)	Mean Atm. CO ₂ (μatm)
Winter	35	671 (74)	0.011 (0.001)	1.645 (0.152)	-5.02 (0.39)	-10.69 (0.79)	404 (16)
Spring	49	744 (146)	0.017 (0.004)	1.733 (0.323)	-5.76 (1.34)	-11.15 (1.16)	402 (18)
Summer	61	544 (133)	0.006 (0.001)	1.331 (0.272)	-4.39 (0.81)	-8.91 (1.84)	405 (25)
Autumn	46	578 (78)	0.011 (0.004)	1.890 (0.203)	-5.08 (0.70)	-10.23 (1.02)	399 (13)
Yearly	190	634 (108)	0.011 (0.003)	1.649 (0.237)	-5.06 (0.81)	-10.25 (1.20)	402 (3)

Note. Values are seasonal means (standard deviations).

Abbreviations: DIC, dissolved inorganic carbon; DOC, dissolved organic carbon; VPDB; Vienna Pee Dee belemnite.

the braided reach (2,800 m); the lowest pCO₂ was sampled in a snowmelt-fed tributary during spring (309 μatm). Of all streamwater samples, 8% were undersaturated in CO₂ with respect to the atmosphere. The undersaturation was observed in nival tributaries in spring (13% undersaturation) and in the reaches closest to the glacier in summer. The sites with CO₂ undersaturation had one commonality: low concentration of calcium ions, low DIC concentrations, and an enriched δ¹³C-CO₂ and δ¹³C-DIC isotopic compositions. A possible explanation for this CO₂ undersaturation is carbonate buffering in the stream, where snow and ice meltwater, low in CO₂, mix with the streamwater. DIC represented the vast majority of the total dissolved carbon (DIC and DOC) in the streamwater (99.0 ± 0.8% across the stream network). Of the DIC species (CO₂, HCO₃⁻, and CO₃²⁻) CO₂ accounted for 2.9 ± 0.6% of the DIC given the high pH (8.14 ± 0.12).

Streamwater DOC concentration averaged 0.011 ± 0.003 mmol C/L in the mainstem across all seasons; it was highest in spring (0.017 ± 0.004 mmol C/L) and lowest in summer (0.006 ± 0.001 mmol C/L). The largest spatial variation in DOC concentration was observed in spring, when DOC concentration in snow-fed tributaries (0.026 ± 0.010 mmol C/L) was up to 66% higher than in the mainstem. Linear regression analysis detected a weak positive relationship between streamwater DOC concentration and pCO₂ for all sites along the mainstem and across all four seasons ($R^2 = 0.17$, $p < 0.0001$); however, when including the tributaries, there was no relation between DOC concentration and pCO₂ ($R^2 = 0.0005$, $p > 0.05$). Streamwater DIC concentration was positively related to pCO₂ across all mainstem sites and seasons ($R^2 = 0.26$, $p < 0.0001$), and across the entire network ($R^2 = 0.33$, $p < 0.0001$). Streamwater DIC concentration was related to pCO₂ in spring ($R^2 = 0.59$, $p < 0.0001$) and summer ($R^2 = 0.42$, $p < 0.0001$), but not in winter and autumn.

Furthermore, the isotopic composition of DIC and CO₂ varied spatially and across seasons (Figure 4). δ¹³C-DIC was negatively related to streamwater pCO₂ for all mainstem sites ($R^2 = 0.49$, $p < 0.0001$), and also for the entire stream network ($R^2 = 0.42$, $p < 0.0001$). δ¹³C-CO₂ was negatively related to streamwater pCO₂ for all mainstem sites ($R^2 = 0.49$, $p < 0.0001$) and for the entire stream network ($R^2 = 0.45$, $p < 0.0001$). The theoretically calculated δ¹³C-CO₂ values (i.e., estimated from DIC concentration, δ¹³C-DIC and temperature) were negatively related to streamwater pCO₂ for all mainstem sites ($R^2 = 0.66$, $p < 0.0001$), and the entire stream network ($R^2 = 0.39$, $p < 0.0001$). In spring, δ¹³C-DIC ($R^2 = 0.68$, $p < 0.0001$), measured δ¹³C-CO₂ ($R^2 = 0.74$, $p < 0.0001$), and calculated δ¹³C-CO₂ ($R^2 = 0.66$, $p < 0.0001$) were all inversely related to pCO₂. Those three parameters were also significantly ($p < 0.0001$) related with pCO₂ in summer ($R^2 = 0.41$, $R^2 = 0.38$, and $R^2 = 0.39$, respectively). No corresponding relationships were observed in winter or autumn.

Change point analyses detected spatial shifts in streamwater pCO₂ and related chemical constituents. In winter, spatial shifts were detected at 1,600 and 2,600 m from the outlet where decreasing streamwater pCO₂ was associated with an increase in pH and enrichment in isotopic compositions of CO₂ and DIC. These changes indicate local upwelling of groundwater delivering CO₂ to the stream. Similarly, in summer, we identified a local increase in streamwater pCO₂ at 3,000 m, which was associated with elevated SC, alkalinity, and calcium concentrations, and with more depleted δ¹³C-CO₂ values. In autumn, decreases in pCO₂ at 2,600 and 300 m were associated with an increase in pH and an enrichment in the isotopic compositions of CO₂ and DIC. Interestingly, this spatial pattern with local upwelling was not pronounced in spring. Rather, there was a gradual increase in pCO₂ along the braided channels (Figure 4), which was associated with increases in streamwater temperature, SC, pH, alkalinity, and calcium concentrations, but also with more depleted isotopic compositions of CO₂ and DIC.

Figure 5. Groundwater contributions were significant positively related to (a) $p\text{CO}_2$ and significantly negatively related to (b) measured $\delta^{13}\text{C}\text{-CO}_2$ and (c) calculated $\delta^{13}\text{C}\text{-CO}_2$ (CO_2 in equilibrium with dissolved inorganic carbon).

3.4. Sources of Streamwater CO_2

Relative groundwater contributions to the streamflow coincided with elevated streamwater $p\text{CO}_2$ for all data pooled across seasons ($R^2 = 0.47$, $p < 0.0001$; Figure 5a); it was not significantly related to streamwater $p\text{CO}_2$ in winter or autumn, but in spring (mainstem: $R^2 = 0.73$, $p < 0.0001$; braided reach: $R^2 = 0.93$, $p < 0.0001$) and in summer (mainstem: $R^2 = 0.66$, $p < 0.0001$; braided reach: $R^2 = 0.66$, $p < 0.01$). Streamwater $p\text{CO}_2$ was inversely related to the relative snowmelt contributions in spring ($R^2 = 0.74$, $p < 0.0001$). Streamwater $p\text{CO}_2$ was also inversely related to the relative glacier ice melt in spring ($R^2 = 0.56$, $p < 0.0001$) and summer ($R^2 = 0.51$, $p < 0.0001$). Across all seasons, relative groundwater contributions were negatively related to streamwater $\delta^{13}\text{C}\text{-DIC}$ ($R^2 = 0.62$, $p < 0.0001$), suggesting groundwater as a major source of DIC. Relative groundwater contributions were also negatively related to streamwater $\delta^{13}\text{C}\text{-CO}_2$ ($R^2 = 0.59$, $p < 0.0001$; Figure 5b) and to the theoretically calculated $\delta^{13}\text{C}\text{-CO}_2$ ($R^2 = 0.68$, $p < 0.0001$; Figure 5c), suggesting that groundwater was also an important CO_2 source to the streamwater.

The results obtained from the Miller-Tans and Keeling linear mixing models suggest that the DIC sources to the streamwater were enriched in ^{13}C . An equal contribution from abiotic CO_2 originating from carbonate bedrock dissolution/precipitation (i.e., 0‰; Clark & Fritz, 1997) and heterotrophic and autotrophic soil respiration (approximated to -21.5‰, calculated from groundwater $\delta^{13}\text{C}\text{-DIC}$ values, DIC concentration, and temperature) would imply a $\delta^{13}\text{C}\text{-DIC}$ value of -10.8‰. However, measured streamwater $\delta^{13}\text{C}\text{-DIC}$ source estimates (from Miller-Tans and Keeling plot averages) deviated from this prediction and changed seasonally from -4.9 to -11.2‰ (Figure 6 and Table 3). Linear mixing suggests that carbonate bedrock weathering likely was the dominant DIC source throughout the year, comprising 72, 48, 66, and 76% of the DIC source in winter, spring, summer, and autumn, respectively. The DIC sources did not only vary temporally. They also varied spatially with DIC in the braided reach being isotopically more depleted in ^{13}C (annual mean of -9.45 ± 0.69 ‰, most ^{13}C depleted in spring with -10.20‰) than the downstream reaches (annual mean -5.57 ± 1.33 ‰, most enriched in autumn with -4.44‰) and upstream reaches (annual mean -4.59 ± 1.34 ‰, most enriched in summer with -3.09‰).

The annual mean isotopic composition of the CO_2 source was -13.23 ± 2.28 ‰ (Miller-Tans) and -13.50 ± 2.56 ‰ (Keeling). The isotopic composition of the source was more enriched in winter (-12.41 ± 1.39 ‰) and autumn (-10.72 ± 2.13 ‰) than in spring (-15.96 ± 0.26 ‰) and summer (-14.37 ± 0.35 ‰; Figure 7 and Table 4). This suggests a relevant contribution of CO_2 from soil respiration to the streamwater across all seasons (58, 74, 67, and 50% in winter, spring, summer, and autumn, respectively). Similar spatial isotopic variation as for the DIC sources could be seen for CO_2 sources, where CO_2 in the braided reach was isotopically more depleted in ^{13}C (annual mean of -15.59 ± 3.58 ‰) than in the downstream (annual mean of -10.47 ± 2.11 ‰) and upstream (annual mean of -10.95 ± 3.07 ‰) reaches. Using linear mixing, we estimated the mean annual contribution of respiratory soil CO_2 to streamwater to 73 ± 0.2 %. However, all above estimates were likely influenced by atmospheric exchange. In fact, the theoretically calculated $\delta^{13}\text{C}\text{-CO}_2$ was more depleted in ^{13}C compared to the measured $\delta^{13}\text{C}\text{-CO}_2$, which suggests that the CO_2 is not in equilibrium with the rest of the DIC species. It also implies that a proportion of the CO_2 measured in the stream may originate from

Figure 6. Estimation of the isotopic composition of the dissolved inorganic carbon (DIC) sources by season (winter, spring, summer, and autumn). The isotopic composition of the carbon source is (a) the slope of the linear regression in the Miller-Tans plot (a) and (b) the intercept with the y axis in the Keeling plot. The Miller-Tans and Keeling plots indicate a DIC source enriched in ^{13}C in winter relative to a more depleted source in spring. In summer, the isotopic composition of the DIC source becomes more ^{13}C enriched, and in autumn, the ^{13}C source composition is similar to the composition in winter. All plots were significant ($p < 0.0001$).

the speciation within the carbonate equilibria, such as weathering-derived carbon with a heavier isotopic composition. Applying the Miller-Tans and Keeling mixing models on the theoretically calculated CO_2 concentrations and isotopic compositions resulted in CO_2 source estimates substantially more depleted in ^{13}C compared to the models applied to the measured values (Miller-Tans: $-19.08 \pm 1.95\text{‰}$; Keeling: -18.97 ± 2.25 ; Figure 7 and Table 4). CO_2 evasion can shift $\delta^{13}\text{C}\text{-DIC}$ isotopic compositions by 1 to 4‰ (Campeau et al., 2018) and thereby bias those estimates. However, a more depleted DIC would reflect an even higher ^{13}C depletion of the CO_2 . Thus, source estimates based on those “preevaded” theoretically calculated $\delta^{13}\text{C}\text{-CO}_2$ revealed that respiratory soil CO_2 most likely contribute to the vast majority of the CO_2 in the streamwater. As estimated by linear mixing from the theoretically calculated $\delta^{13}\text{C}\text{-CO}_2$ values, the mean annual contribution of respiratory soil CO_2 to streamwater CO_2 was $88 \pm 0.1\%$, while the remaining CO_2 originated from weathered products by conversion of HCO_3^- to CO_2 due to the speciation within the carbonate equilibria.

3.5. Fate of the Streamwater CO_2

We observed a longitudinal pattern in streamwater $\delta^{13}\text{C}\text{-CO}_2$ with more depleted values in the braided reach compared to those downstream from the valley nexus (Figure 4). $\delta^{13}\text{C}\text{-CO}_2$ became rapidly enriched (on average $6.9 \pm 1.3\text{‰}$) within 500 m downstream from the braided reach. Across all seasons, the source of

Table 3
Equations and DIC Source Estimates Obtained From the Miller-Tans and Keeling Plots

Season	Model	<i>n</i>	Equation	DIC source (‰VPDB)	R^2	Std. error	<i>p</i> -value
Winter	Miller-Tans	35	$\delta^{13}\text{C}\text{-DIC} \times [\text{DIC}] = -4.72 \times [\text{DIC}] - 0.49$	-4.72	0.54	0.76	<0.0001
	Keeling		$\delta^{13}\text{C}\text{-DIC} = 0.21 \times 1/[\text{DIC}] - 5.15$	-5.15	0.0009	0.76	<0.0001
Spring	Miller-Tans	49	$\delta^{13}\text{C}\text{-DIC} \times [\text{DIC}] = -10.96 \times [\text{DIC}] + 8.66$	-10.96	0.94	0.40	<0.0001
	Keeling		$\delta^{13}\text{C}\text{-DIC} = 9.43 \times 1/[\text{DIC}] - 11.42$	-11.42	0.80	0.42	<0.0001
Summer	Miller-Tans	61	$\delta^{13}\text{C}\text{-DIC} \times [\text{DIC}] = -7.40 \times [\text{DIC}] + 3.83$	-7.40	0.91	0.31	<0.0001
	Keeling		$\delta^{13}\text{C}\text{-DIC} = 3.85 \times 1/[\text{DIC}] - 7.42$	-7.42	0.67	0.28	<0.0001
Autumn	Miller-Tans	46	$\delta^{13}\text{C}\text{-DIC} \times [\text{DIC}] = -5.39 \times [\text{DIC}] + 0.59$	-5.39	0.40	0.99	<0.0001
	Keeling		$\delta^{13}\text{C}\text{-DIC} = -0.14 \times 1/[\text{DIC}] - 5.01$	-5.01	0.0002	0.81	<0.0001

Note. The standard errors and *p*-values represent the accuracy of the slopes (Miller-Tans) and intercepts (Keeling). Abbreviation: DIC, dissolved inorganic carbon.

Figure 7. Estimation of the isotopic composition of the CO_2 sources by season (winter, spring, summer, and autumn). Measured $\delta^{13}\text{C}\text{-CO}_2$ (full symbols) were higher than $\delta^{13}\text{C}\text{-CO}_2$ calculated from $\delta^{13}\text{C}\text{-dissolved inorganic carbon (DIC)}$, DIC concentration, and temperature (open symbols). The annual mean isotopic composition of the CO_2 source, predicted by (a) Miller-Tans and (b) Keeling plots, were $-13.36 \pm 2.35\text{‰}$ and $-19.02 \pm 2.04\text{‰}$ for the measured and calculated $\delta^{13}\text{C}\text{-CO}_2$ source respectively. All plots were significant ($p < 0.0001$).

CO_2 in the mainstem was generally enriched by 1.62‰ (estimated from measured $\delta^{13}\text{C}\text{-CO}_2$) and 1.73‰ (estimated from calculated $\delta^{13}\text{C}\text{-CO}_2$; $p < 0.0001$ for all seasons) compared to the braided reach; this translates into an enrichment by 10 and 8%, for the measured and calculated samples, respectively. Similarly, there was a ^{13}C enrichment of the DIC source downstream of the groundwater discharge zone (on average by 1.7‰ for the Miller-Tans and Keeling plots, $p < 0.0001$ for all seasons). The difference in isotopic compositions (both $\delta^{13}\text{C}\text{-CO}_2$ and $\delta^{13}\text{C}\text{-DIC}$) between the braided reach and downstream reaches can be attributed to the loss of ^{12}C due to CO_2 evasion. In fact, the ^{13}C enrichment downstream from the groundwater upwelling zone in the braided reach (where isotopic data suggest additions of biogenic carbon to the stream) coincided with a decrease in $p\text{CO}_2$ (12 to 27% within 500 m downstream from the braided reach) and a simultaneous increase in pH (with 2.1 to 2.9%). This implies a loss of CO_2 and a subsequent shift in the carbonate equilibria.

Due to the high channel slope (0.093 ± 0.033 m/m) and high-flow velocity ($0.51\text{--}0.79$ m/s), we found areal CO_2 evasion fluxes, which were on average eight times higher as those reported from other headwater streams (Table 5). In fact, areal CO_2 evasion fluxes averaged across the entire stream network 32.1 ($19.1\text{--}45.9$), 48.9 ($29.1\text{--}69.9$), 17.8 ($10.6\text{--}25.5$), and 21.7 ($12.9\text{--}31.0$) $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ in winter, spring, summer, and autumn, respectively. Across all seasons, this gives a mean CO_2 evasion flux of 30.1 ($18.0\text{--}43.1$) $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ (Table 5). However, areal CO_2 evasion fluxes were even higher in the reaches with significant

Table 4

Estimate of the CO_2 Source Isotopic Compositions Obtained From the Miller-Tans and Keeling Plots

CO_2 data	Season	Miller-Tans		Keeling		Mean ($\pm$ std.)
		Slope $\delta^{13}\text{C}\text{-CO}_2 \times [\text{CO}_2]$ versus $[\text{CO}_2]$	Slope $\delta^{13}\text{C}\text{-CO}_2 \times [\text{DIC}]$ versus $[\text{DIC}]$	Intercept $\delta^{13}\text{C}\text{-CO}_2$ versus $1/[\text{CO}_2]$	Intercept $\delta^{13}\text{C}\text{-CO}_2$ versus $1/[\text{DIC}]$	CO_2 source (‰VPDB)
Measured	Winter	-11.97	-12.85	-10.77	-14.05	-12.41 (± 1.39)
	Spring	-15.79	-15.71	-16.29	-16.03	-15.96 (± 0.26)
	Summer	-14.09	-14.11	-14.83	-14.43	-14.37 (± 0.35)
	Autumn	-12.55	-8.75	-12.56	-9.00	-10.72 (± 2.13)
Calculated	Winter	-18.35	-17.01	-17.76	-17.21	-17.58 (± 0.60)
	Spring	-20.28	-23.12	-20.86	-23.54	-21.95 (± 1.62)
	Summer	-18.94	-19.45	-18.31	-19.42	-19.03 (± 0.53)
	Autumn	-17.49	-17.96	-16.86	-17.76	-17.52 (± 0.48)

Note. Both the CO_2 concentrations and the total dissolved inorganic carbon concentrations were used to reduce potential errors caused by decreasing concentrations due to loss of CO_2 to the atmosphere. All plots were significant ($p < 0.0001$).

Table 5
Comparison of $p\text{CO}_2$ and CO_2 Evasion Rates From Headwater Streams

Location	$p\text{CO}_2$ (μatm)	CO_2 flux ($\mu\text{mol C} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	Reference
Switzerland, Alpine stream	634	30.1	This study
Austria, Alpine streams	794	3.12	Schelker et al. (2016)
Alaska, USA, boreal stream	1417	5.21	Crawford et al. (2013)
Wyoming, USA, alpine streams	391	-0.02	Kuhn et al. (2017)
Tibetan Plateau, China, high-altitude rivers	982	5.16	Qu et al. (2017)
Loess Plateau, China, river	1068	1.86	Ran et al. (2017)
Sweden, first-order streams	1445	8.00	Humborg et al. (2010)

groundwater upwelling. For instance, in spring, we calculated CO_2 evasion fluxes from the braided stream reach to be more than 15-fold higher ($477 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) compared to the seasonal mean. We estimated the mean areal CO_2 evasion fluxes from the entire stream network at 237 (141–339), 2793 (1069–2565), 299 (179–428), and 344 (205–493) kg C/day for winter, spring, summer, and autumn, respectively. These fluxes translate into an annual CO_2 evasion flux of 244 (145–349) tons of C from the entire stream network. We estimate an average DIC export flux to be in the same order of magnitude as the CO_2 evasion flux (115, 1692, 302, and 327 kg C/day for winter, spring, summer, and autumn, respectively); this translates into an annual DIC export flux of 222 tons of C from the entire stream network.

4. Discussion

High-resolution spatial sampling revealed the importance of catchment geomorphology and stream network expansion and contraction for streamwater $p\text{CO}_2$ and CO_2 evasion dynamics in an Alpine headwater stream. Catchment geomorphology is characterized by steep valley slopes confining a wide valley bottom with braided stream channels, which transit into a canyon-like channel contained within a constrained valley. This geomorphological shift caused significant groundwater upwelling thereby increasing downstream discharge. We argue that this upwelling front constitutes a control point (in the sense of Bernhardt et al., 2017) that disproportionately controls stream ecosystem processes and biogeochemistry. Our results highlight the variability of such a control point in space and time as associated with the seasonal expansion and contraction of the stream network, following the nivo-glacial hydrological regime. The influence of the control point was most pronounced during spring snowmelt when hydrological connectivity through various subsurface and surface flow paths increased stream network expansion with marked implications for streamwater biogeochemistry.

Across all seasons, the carbonate rock that dominates the catchment geology markedly contributed to streamwater DIC as indicated by its isotopic composition of -7‰. Elevated streamwater DIC concentration and hence elevated pH shifted the carbonate equilibrium toward bicarbonate and carbonate species. Thus, despite high DIC concentration, the streamwater remained only slightly supersaturated in CO_2 with respect to the atmosphere. Our findings suggest that streamwater CO_2 originates mostly from soil respiration; this is in line with findings from a boreal stream network (e.g., Campeau & del Giorgio, 2014), and small North American (Crawford et al., 2015) and Amazonian headwater streams (Johnson et al., 2008). Our findings also agree with those from Butman and Raymond (2011) reporting high contributions from soil respiration to CO_2 evasion fluxes from streams and rivers in the conterminous United States, where soil respiration contributed with 17–25% to the evasion flux from streams and rivers, and up to 90% from first-order streams. Our observations are also supported by previously reported respiration rates in the soils adjacent to the braided stream reaches (2,800 m). In fact, Grand et al. (2016) measured soil respiration rates in this area, which were twice as high as the average ($10 \mu\text{mol C} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) in the Vallon de Nant catchment.

During stream network expansion, increasing groundwater upwelling can deliver more respiratory CO_2 from the soils to the stream. In contrary, our results suggest that direct snowmelt transported by surface runoff did not contribute to streamwater $p\text{CO}_2$ nor did snowmelt increase streamwater DOC concentration, as was previously reported from other studies (e.g., Sommerfeld et al., 1991). Contrary to previous findings from boreal streams, rivers, and lakes (Campeau & del Giorgio, 2014; Lapierre et al., 2013), we did not find any clear evidence that streamwater DOC could contribute to $p\text{CO}_2$ through ecosystem respiration.

We suggest that the remarkably low DOC concentrations together with low residence times typical for high-altitude and high-slope streams and high CO₂ evasion rates make it difficult to detect and quantify CO₂ originating from stream ecosystem respiration. We used a mass balance approach to trace the potential contribution of stream ecosystem respiration to the streamwater $\delta^{13}\text{C}$ -DIC composition. To estimate $\delta^{13}\text{C}$ -DOC values, we subtracted 20‰ from the $\delta^{13}\text{C}$ -DIC (e.g., Clark & Fritz, 1997). Next, we inferred from mass balance equations (e.g., equation (1), rewritten as the isotopic composition multiplied with concentration for DIC, DOC, and DIC+DOC) that DOC could potentially enrich the $\delta^{13}\text{C}$ -DIC by $0.14 \pm 0.07\text{‰}$. To enrich $\delta^{13}\text{C}$ -DIC by 1‰, an additional 0.08 ± 0.02 mmol/L DOC would be required. This additional DOC would translate into an increase in the annual mean DOC concentration by 86.4%. This approximation suggests that stream ecosystem respiration contributed only marginally to the observed streamwater $p\text{CO}_2$, which is in general agreement with results from a large spatial survey on the CO₂ dynamics in streams throughout the United States (Hotchkiss et al., 2015). We argue that this apparent difference is attributable to both low biomass and low residence times typical for high-altitude and high-slope streams.

We do acknowledge that our approach based on stable isotopes can be considered as an approximation alone and is prone to large uncertainties. Furthermore, the rapid evasion of groundwater-derived CO₂ from the stream may lead to erroneous estimates of streamwater CO₂ concentration and isotopic composition as grab samples may represent streamwater that is already degassed (e.g., Deirmendjian & Abril, 2018). Rapid CO₂ evasion may explain the concordance between the calculated “preevasion” streamwater $\delta^{13}\text{C}$ -CO₂ and the measured values in groundwater, and between the measured streamwater $\delta^{13}\text{C}$ -CO₂ and atmospheric $\delta^{13}\text{C}$ -CO₂.

The high CO₂ evasion fluxes from the stream network were unexpected given that high-altitude streams typically have low $p\text{CO}_2$ and therefore low CO₂ evasion fluxes (Crawford et al., 2015). Our high-resolution sampling along the stream network identified local groundwater upwelling as a significant contributor to the areal annual CO₂ evasion fluxes. Control points mediated by the local geomorphology induced CO₂ evasion rates that were up to 60 times higher than those reported for boreal first-order streams (Humborg et al., 2010). This is remarkable given that the overall streamwater $p\text{CO}_2$ was lower than in most boreal streams (Crawford et al., 2013; Humborg et al., 2010). Rather, streamwater $p\text{CO}_2$ in the Vallon de Nant catchment was often close to atmospheric equilibrium and bracketed by values reported from other high-altitude streams in Austria (Schelker et al., 2016), United States (Kuhn et al., 2017), and China (Qu et al., 2017; Ran et al., 2017). Although the Vallon de Nant catchment stream network CO₂ evasion fluxes were orders of magnitude higher than those found in other high-altitude streams (Table 5), this difference was likely due to the high contribution of CO₂ from the control point along the stream network, along with the high gas-exchange. Therefore, higher gas transfer velocity rates rather than increased streamwater $p\text{CO}_2$ drove the observed high evasion rates within the braided reach. We acknowledge that our estimates of CO₂ evasion rates may be biased by incorrect model assumptions of the gas transfer velocity model, but since there are only very few models established for high-energy mountain streams, we consider applying the gas transfer velocity model from Ulseth et al. (2019) to be more accurate than applying models established from large low-land rivers, such as one of the commonly used equations from Raymond et al. (2012). Crawford et al. (2015) found the opposite pattern, where the equations from Raymond et al. (2012) may have led to an overestimation of the CO₂ evasion fluxes. However, the region studied in that paper was significantly different from the stream network in this study; due to the carbonate bedrock and the inputs from soil respiration, our stream network was most likely not limited by supply, as the streams studied in Crawford et al. (2015) where the streamwater $p\text{CO}_2$ commonly indicated undersaturation. In our study, streamwater CO₂ supersaturation within the braided reach, despite high gas transfer velocity rates, highlights the role of groundwater upwelling for the CO₂ delivery into the stream.

Our spatially highly resolved sampling allowed us to capture small-scale variations in streamwater $p\text{CO}_2$ and to detect control points driving CO₂ evasion fluxes at the scale of the stream network. Grab samples confined to a few individual reaches may underestimate the actual evasion fluxes at the network scale. This finding corroborates a recent study by Duvert et al. (2018) highlighting the relevance of groundwater for the CO₂ dynamics in temperate, boreal, and tropical streams.

Headwater streams comprise most of the drainage length in fluvial networks (Downing et al., 2012) and can expand and contract as a response to catchment hydrology (Godsey & Kirchner, 2014). These properties have major implications for the exchange fluxes at the terrestrial-aquatic interface (e.g., Williamson et al., 2008), especially when considering the diverse surface and subsurface flow paths connecting the stream to its terrestrial environment in small catchments (Fisher et al., 2014). Understanding the implications of this hydrological connectivity on stream biogeochemistry may therefore contribute to an enhanced understanding on spatial and temporal variability of CO₂ sources and evasion fluxes (Allen et al., 2018; Duvert et al., 2018). In the Vallon de Nant catchment, the stream network covered a four times larger surface area during the expansion in spring (35,300 m²) compared to winter (7,100 m²). Network expansion during spring snowmelt increased the hydrological connectivity to the groundwater and thereby the delivery of CO₂ from soil respiration and calcareous rock weathering that has likely accumulated during winter under the snowpack (similar as suggested by Duvert et al., 2018). At the same time, the magnification of the stream surface area at the interface to the atmosphere in combination with increased discharge (and turbulence) increased the CO₂ evasion flux to be 10 times larger in spring compared to winter.

Our results on the role of stream network dynamics for CO₂ sources and evasion also emphasize that we need to better apprehend the lateral carbon flux across the terrestrial-aquatic interface (Regnier et al., 2013), which is at the basis of the “boundless carbon cycle” across ecosystem boundaries (Battin et al., 2009). This is imperative to understand future impacts of climate change on ecosystem processes and biogeochemistry of high-altitude streams. In fact, climate-induced changes of catchment hydrology are expected to impact the movement of inorganic and organic carbon from the terrestrial environment to streams (Tank et al., 2018). Owing to the low soil buildup and the prevalence of bare rock, the terrestrial delivery of inorganic carbon species dominates over DOC deliveries to streams in high-altitude catchments — a relationship that may change in the future as vegetation cover moves uphill. This consideration would also imply an integrative view of the speciation of CO₂, HCO₃[−], and CO₃^{2−} within the carbonate system to better quantify and predict the carbon balance at catchment level (Tank et al., 2018). For instance, in the Vallon de Nant catchment, streamwater CO₂ constituted on average only 2.9% of the DIC pool, most likely because of an average pH of 8.14. Downstream transformation of HCO₃[−] to CO₂ because of pH shifts could impact CO₂ evasion rates and hence the carbon balance of the stream.

In summary, our high-resolution spatial sampling over four seasons enabled us to capture the relevance of stream network expansion and contraction and of a control point for the streamwater CO₂ dynamics in a high-altitude catchment. Despite low streamwater pCO₂, our results suggest that high-altitude streams are potential sources of CO₂ to the atmosphere. Our findings further contribute to the understanding of the biogeochemistry of glacier-fed streams now changing rapidly because of climate change (Milner et al., 2017).

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