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Dynamics and potential drivers of CO$_2$ concentration and evasion across temporal scales in high-alpine streams

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Abstract

Carbon dioxide (CO$_2$) evasion from streams greatly contributes to global carbon fluxes. Despite this, the temporal dynamics of CO$_2$ and its drivers remain poorly understood to date. This is particularly true for high-altitude streams. Using high-resolution time series of CO$_2$ concentration and specific discharge from sensors in twelve streams in the Swiss Alps, we studied over three years the responsiveness of both CO$_2$ concentration and evasion fluxes to specific discharge at annual scales and at the scale of the spring freshet. On an annual basis, our results show dilution responses of the streamwater CO$_2$ likely attributable to limited supply from sources within the catchment. Combining our sensor data with stable isotope analyses, we identify the spring freshet as a window where source limitation of the CO$_2$ evasion fluxes becomes relieved. CO$_2$ from soil respiration enters the streams during the freshet thereby facilitating CO$_2$ evasion fluxes that are potentially relevant for the carbon fluxes at catchment scale. Our study highlights the need for long-term measurements of CO$_2$ concentrations and fluxes to better understand and predict the role of streams for global carbon cycling.

1. Introduction

Inland waters are now recognized as important components of the global carbon cycle (Cole et al 2007, Battin et al 2009, Drake et al 2018) with total carbon (C) evasion fluxes to the atmosphere possibly as high as 3.88 Pg C yr$^{-1}$ (Drake et al 2018). Among the inland waters, headwater streams—the smallest but most abundant streams in fluvial networks—are estimated to contribute approximately one third to the global carbon dioxide (CO$_2$) evasion flux (Marx et al 2017). Our understanding of the role of headwater streams for large-scale carbon fluxes is largely based on the study of headwater streams draining biomes with large carbon stocks (Johnson et al 2008, Wallin et al 2013, Lauerwald et al 2015) and generally attributed to the close connectivity with the terrestrial environment, which delivers large amounts of carbon, including CO$_2$ from soil respiration, to the headwaters (Hotchkiss et al 2015, Tank et al 2018). However, not all headwater catchments are rich in organic carbon, which is particularly true for mountain catchments above the tree line.

Discharge is a master variable controlling ecological and biogeochemical processes in stream ecosystems. At catchment scale, the response of streamwater solute concentrations (C) to discharge (Q), or specific discharge (q) (here we use $q$ for the sake of cross-catchment comparability), provides information on the sources of solutes within the catchment, their size and arrangement, and mobilization and transport to the streams (e.g. Godsey et al 2009, Meybeck and Moatar 2012). Invariant responses of $C$ to $q$ are indicative of chemostasis and may reflect a uniform distribution of solutes within the catchment (e.g. in soils), where changes in hydrological connectivity and flow-paths position do not alter C in the streamwater. Chemostatis may also be linked to mineral weathering and its associated processes (e.g. Clow and Mast 2010). Chemodynamic responses indicates a change of C
with \( q \), where increasing \( q \) can either dilute or concentrate a solute in the streamwater. Responses of \( C \) to \( q \) are typically described by a simple power function, \( C = aq^b \), where the exponent \( b \) indicates whether the response is chemostatic \((b = 0)\) or chemodynamic (concentration: \( b > 0 \); dilution: \( b < 0 \)) (e.g. Godsey et al 2009, Meybeck and Moatar 2012).

This approach has been widely used to understand event-scale (e.g. storms) behavior of solutes and more recently also inter-annual solute dynamics in streams, and to infer drivers (e.g. source versus transportation limitation) that act at catchment scale (e.g. Godsey et al 2009, Meybeck and Moatar 2012). Numerous studies have focused on the behavior of conservative solutes, including dissolved ions, but few have adopted the \( C-q \) scaling approach to gases, such as \( CO_2 \) (Liu and Raymond 2018), to understand their temporal and spatial dynamics. Unlike non-gaseous solutes that are transported downstream through advective flow, \( CO_2 \) may not only be converted to other carbonate species such as \( HCO_3^- \), but may also be outgassed vertically from the streamwater into the atmosphere (figure 1).

The \( CO_2 \) evasion flux \((F_{CO_2})\) depends on the gas exchange velocity \((k_{CO_2})\) and the gradient between atmospheric and streamwater \( CO_2 \) concentrations. Streamwater \( CO_2 \) concentration and \( F_{CO_2} \) are mutually dependent because (at oversaturation) the latter can deplete the \( CO_2 \) pool within the stream through atmospheric loss, which in turn can diminish \( F_{CO_2} \) (Rocher-Ros et al 2019). This relationship is further complicated by the dual role of \( q \). As shown above, \( q \) drives solute dilution and concentration behavior in streams and at the same time it influences the gas exchange velocity through the water surface (Raymond et al 2012, Ulseth et al 2019). A recent survey by Liu and Raymond (2018) shows that roughly 50% of the streams and rivers throughout the USA had positive responses of \( CO_2 \) concentration to \( q \), which would suggest increased \( CO_2 \) deliveries from the catchment out-balancing \( F_{CO_2} \) from these systems. This is in line with observations that hydrological connectivity, as encapsulated by changes in \( q \) and its relationship with groundwater, can affect the transportation of \( CO_2 \) from various sources (e.g. soil respiration, geogenic origin) within the catchment to the streams (Hotchkiss et al 2015, Duvert et al 2018, Horgby et al 2019) (figure 1).

Based on the previous considerations, we present a framework based on the relationship between the responsiveness of \( CO_2 \) concentration to \( q (b_C) \) and the responsiveness of \( F_{CO_2} \) to \( q (b_F) \), with the aim to gain mechanistic understanding of the dynamics of \( CO_2 \) evasion from streams and its linkage to processes operating at catchment scale (figure 1). An underlying premise to this is that \( F_{CO_2} \) scales with \( q \) similarly as \( C \). That is, a \( b_F > 0 \) would indicate a responsiveness of \( F_{CO_2} \) owing to increasing gas exchange velocity,
possibly also because of no CO2 limitation in the streamwater. A \( b_F < 0 \) would indicate that CO2 depletion in the streamwater in combination with high gas exchange velocity would drive the responsiveness of \( F_{CO2} \) to \( q \). We postulated that low responsiveness of both CO2 concentration and \( F_{CO2} \) to \( q \) would limit \( F_{CO2} \) through low CO2 concentration (i.e. dilution) as it happens for instance when CO2 from terrestrial deliveries and/or in-stream respiration are reduced. Alternatively, CO2 dilution but high \( F_{CO2} \) responsiveness to \( q \) indicates enhanced \( F_{CO2} \) with low CO2 concentrations but high turnover. On the other hand, high responsiveness of both CO2 concentration and \( F_{CO2} \) to \( q \) also enhances \( F_{CO2} \) but because of elevated CO2 concentrations in the streamwater. Our conceptual framework serves as guidance to understand the balance between CO2 supply to the stream and its outgassing from the stream, which ultimately affects the role of streams for large-scale CO2 fluxes (Liu and Raymond 2018, Rocher-Ros et al 2019).

Despite the fact that mountains cover one fourth of the world’s land surface (Kapos et al 2000, Meybeck et al 2001), the CO2 emission fluxes from mountain streams, including their drivers, remain poorly understood to date (Crawford et al 2015, Horby et al 2019, Ulseth et al 2019). In this study, we use high-resolution temporal data over two consecutive water years to assess the CO2 dynamics across a range of twelve streams in the Swiss Alps across different timescales. On a yearly basis, we anticipated an overall limitation on the supply of CO2 from the sources within the catchments, as they are often devoid of major vegetation coverage and soil horizons rich in organic carbon. We also expected low streamwater CO2 concentrations resulting from the combination of low CO2 supply and high gas exchange velocities. Furthermore, we postulate that there are windows when supply limitation becomes relieved, and streams receive larger deliveries of CO2 from sources within the catchment, which would increase the responsiveness of both CO2 concentrations and \( F_{CO2} \). We complemented sensor data with occasional measurements of the isotopic composition of CO2 to explore its potential sources. Our findings shed new light on the CO2 dynamics in high-altitude streams, further contributes to a better understanding of the role of these ecosystems for global carbon fluxes.

2. Methods

2.1. Study streams

We studied twelve streams distributed over four catchments (Valsorey, Champéry, Ferret and Vallon de Nant) in the Swiss Alps and that were selected to cover environmental gradients typical for high-altitude systems (figure S1, table S1 is available online at stacks.iop.org/ERL/14/124082/mmedia). Five streams did not have any glacial influence (PEU, VID, VIM, VIU, and VEL), while seven streams were glacier-fed with glacier coverage ranging from 2 to 27% (VAD: 22%, VAI: 27%, FED: 2%, FEU: 4%, RIC: 6%, AND: 5%, and ANU: 7%). The drainage areas varied in size from 0.3 to 20 km². The average catchment altitude ranged from 1200 to 2161 m above sea level (a.s.l.); stream channel slopes ranged from 0.05 to 0.16 mm⁻¹. Catchment lithologies are dominated by carbonate sedimentary rocks (Champéry and Vallon de Nant) and metamorphic rocks (Valsorey and Ferret) (Hartmann and Moosdorf 2012). Eight of the stream sites were located above the tree line, while the other four streams drained partially forested catchments (VID 0.5%, RIC 1.2%, AND 2.0%, ANU 0.3%). Vegetation cover ranged from 25% to 100%, and bare rocks from 0% to 56% (Boix Canadell et al 2019). Vegetation cover decreased with increasing altitudes both for the glacierized sites \( R^2 = 0.47, n = 7, P = 0.09 \) and the non-glacierized sites \( R^2 = 0.84, n = 5, P < 0.05 \). Streamwater DOC concentrations were low and ranged between 111 and 448 µg C L⁻¹ (Boix Canadell et al 2019).

2.2. High-frequency measurements and isotope sampling

In each stream, we measured streamwater \( pCO_2 \), temperature and depth, as well as barometric pressure every 10 min across three years. We prepared the \( pCO_2 \) sensors (Vaisala CARBOCAP®, GMT220, Vantaa, Finland) according to Johnson et al (2010), where sensors were contained within a polytetrafluoroethylene (ePDFE) semi-permeable membrane sealed with liquid electrical tape. Sensors were further protected with a metal casing and powered by a solar panel. Sensors were maintained and data downloaded on average every month. Raw data were corrected according to the manufacturer’s recommendations for streamwater temperatures (HOBO U24-001 Conductivity Logger, ONSET, Bourne, USA) and barometric pressure (Track-It™ Logger, Monarch Instrument, Amherst, USA), as well as for hydrostatic pressure differences caused by varying water depths. Before deployment, we tested all \( pCO_2 \) sensors in the laboratory using certified gas mixtures of CO2 diluted in synthetic air to final concentrations of 0, 400 and 2000 ppmv. We also performed a laboratory calibration with two of our sensors, which revealed sensor accuracy of −5% and sensor response times between 2.5 and 13 min.

Water depth (Odyssey® Logger, Dataflow Systems Ltd, New Zealand; TruTrack Data Logger, Intech Instruments LTD, New Zealand) was converted to Q from sodium chloride (NaCl) slug additions (Gordon et al 2004). Thereby, we established rating curves for each individual stream (ranging from 4 to 13 NaCl additions in FED and VID, respectively, with an average of 7). From the rating curves, we obtained discharge, which we converted to \( q \) by normalizing for drainage area. Using the same approach, we also
established rating curves between \( Q \) and streamwater velocity \( (V, \text{m} \text{s}^{-1}) \) for each site. We determined stream channel slopes \( (S, \text{mm} \text{m}^{-1}) \) with a dGPS, and the catchment area in ArcGIS 10.5 (Environmental Systems Research Institute, USA) from a 2 m² digital elevation model (Geodata, Swisstopo).

When accessible, streams were sampled on a monthly basis for the determination of the isotopic composition of streamwater CO₂ \( (\delta^{13} \text{C}-\text{CO₂}) \) expressed as ‰ VPDB; Vienna Pee Dee Belemnite) using glass vials sealed with rubber stoppers and metal caps. Samples were stored in the dark (4 °C) pending analyses within 24 h. In the laboratory, we created a headspace (in the 60 ml sample vials) with synthetic air, shook the samples (2 min) and let them equilibrate (2 h). We measured CO₂ concentrations and \( \delta^{13} \text{C} \)-CO₂ using a cavity ring-down spectrometer (Model G2201-I, Picarro Instruments, Santa Clara, CA, USA). Samples for atmospheric CO₂ were collected next to the study streams into glass vials sealed with rubber stoppers and metal caps; we injected additional 50 ml of ambient air to over-pressurize the samples, which were measured on the same Picarro G2201-I as above.

### 2.3. CO₂ concentration and evasion flux calculations

At the 10 min basis, we multiplied monitored streamwater \( p\text{CO}_2 \) with Henry’s constant \( (K_H, \text{mol} \text{m}^{-1} \text{atm}^{-1}) \) (Plummer and Busenberg 1982) as a function of streamwater temperature and atmospheric pressure \( (P_{\text{atm}}, \text{atm}) \) to obtain streamwater CO₂ concentration. \( F_{\text{CO}_2} \) were calculated from the CO₂ gradient \( (\Delta \text{CO}_2, \text{mol} \text{m}^{-1}) \) between the streamwater and the atmosphere, and the gas transfer velocity for CO₂ \( (k_{\text{CO}_2}, \text{m} \text{d}^{-1}) \) (equation (1)).

\[
F_{\text{CO}_2} = k_{\text{CO}_2} \times \Delta \text{CO}_2
\]

To estimate \( \Delta \text{CO}_2 \), we first derived site-specific time series of atmospheric CO₂ from the air samples that we had collected in proximity of the streams (in average 11 measurements per stream; minimum 5, maximum 16), using linear interpolation between sampling dates. The atmospheric CO₂ was multiplied with \( K_H \) and \( P_{\text{atm}} \) at 10 min time steps to obtain atmospheric CO₂ concentrations at saturation \( (\text{CO}_2_{sat}, \text{mol} \text{m}^{-1}) \). We subtracted \( \text{CO}_2_{sat} \) from the streamwater CO₂ concentrations to obtain \( \Delta \text{CO}_2 \).

Ulseth et al (2019) recently described gas transfer velocities \( (k_{600}, \text{m} \text{d}^{-1}) \) in turbulent mountain streams as function of energy dissipation \( (eD, \text{m}^2 \text{s}^{-3}); \) turbulent stream: \( eD > 0.02 \text{m}^2 \text{s}^{-3} \), where \( eD \) is calculated as a function of stream flow velocity, stream channel slope and gravity acceleration \( (g, \text{m} \text{s}^{-2}) \) (the three variables are multiplied).

\[
k_{600} = \exp^{6.43+1.18 \times \ln(eD)}
\]

We converted \( k_{600} \) to \( k_{\text{CO}_2} \) (m d⁻¹) (equation (3)) using the Schmidt scaling (Wanninkhof 2014), as shown in equation (4).

\[
k_{\text{CO}_2} = \frac{k_{600}}{600}^{0.5}
\]

\[
S_{\text{CO}_2} = 1923.6 - 125.06 \times T_w + 4.3773 \times T_w^2
- 0.085 \times T_w^3 + 0.00070284 \times T_w^4
\]

We performed all sensor corrections and flux calculations in Matlab R2017b.

#### 2.4. Data analyses

We analyzed time series covering two water years (defined according to the US Geological Survey as a time period ranging from 1 October to 30 September) using data for a period from 1 October 2016 to 30 September 2018, in order to capture two snowmelt periods, as well as two ‘freshet’ periods. We define the freshets as the first flushing events during the onset of the snowmelt. We collapsed the 10 min interval data from the time series to daily median values of CO₂ concentration, \( q \) gas transfer velocity of CO₂ \( (k_{\text{CO}_2}) \) and \( F_{\text{CO}_2} \). We followed the same approach as Liu and Raymond (2018) to identify the responses of CO₂ concentration, \( k_{\text{CO}_2} \) and \( F_{\text{CO}_2} \) to \( q \), respectively. We used power law functions with transformed data (log (x + 50)) to analyze whether the responses were chemostratic or chemodynamic, as well as the magnitude of the response (Godsey et al 2009, Meybeck and Moatar 2012). We fitted the data using partial least squares regressions. We fitted each site and each water year separately, for which we derived statistical parameters. We used \( \alpha = 0.05 \) as the threshold for statistical significance and the coefficient of determination, \( R^2 \), to determine the goodness of the fit. We used JMP 13 (SAS Institute Inc., Cary, USA) for all statistical analyses.

### 3. Results and discussion

#### 3.1. Hydrological regimes

The hydrological regimes of our study streams are typical for high-altitude systems (Hannah et al 2005, Milner et al 2009). After an extended winter baseflow, where \( q \) was relatively stable, the snowmelt period started between March and April depending on the altitude and exposition of the catchments. Snowmelt further shaped the hydrological regimes throughout spring and summer. As expected, \( q \) in summer was higher in the glacier-fed streams due to the glacier ice melt. The 2016/2017 winter was milder with less precipitation than the 2017/2018 winter, which resulted in overall higher spring and summer \( q \) in the water year of 2018 (figure S2).

#### 3.2. Streamwater CO₂ concentration dynamics

Overall, we found low streamwater CO₂ concentrations (figure S2), which is consistent with other reports on similar streams (e.g. Schelker et al 2016, Kuhn et al 2017, Qu et al 2017, Horgby et al 2019). At a 10 min
basis, median CO₂ concentrations ranged from 22.0 to 36.7 μmol l⁻¹ across all study streams during both water years (table S1), with 6.5 and 77.6 μmol l⁻¹ as minimum and maximum concentrations, respectively. Daily median CO₂ concentrations covered a similar range as the 10 min time step (ranging from 21.8 to 36.0 μmol l⁻¹ across all study streams and both water years). Therefore, we used the daily median for all further analyses, which would also smooth potential outliers and make estimates more robust. Despite often incomplete time series owing to sensor malfunctioning or loss (average data coverage across the two water years of 41%; minimum data coverage of 23% at PEU; maximum data coverage of 62% at VAU), our analysis of streamwater CO₂ concentration revealed recurrent seasonal patterns. Specifically, the CO₂ concentrations increased during the recession of the snowmelt and ice melt and further into fall baseflow. The freshet (i.e. onset of the snowmelt period) in early spring was marked by a transient increase in both q and CO₂ concentration in several of our streams (e.g. VAD, VAU, VIM, FED, AND, ANU).

### 3.3. Annual responsiveness of CO₂ concentration and evasion fluxes to specific discharge

On an annual basis, we consistently found inverse relationships between CO₂ concentration and q with a median b_C of −0.09 and ranging between −0.27 and 0.17 across streams. Only two C–q relationships (from VEL 2018 and VIM 2018) yielded non-significant statistic. There were only two significant positive b_C (VIU 2017: 0.04 ± 0.004; FEU 2017: 0.17 ± 0.025), however for FEU in 2017 it may be attributable to the relatively low number of daily concentration data (n = 55). Across the 22 significant C–q relationships, three of the study streams (VIU, RIC, ANU) showed near-chemostatic behavior defined as b_C = −0.05 to 0.15 according to Godsey et al (2009) during one and/or two of the studied water years (figure 2, table S2). For instance, RIC showed near-chemostatic behavior in 2017 (b_C = −0.04 ± 0.002) but a more pronounced chemodynamic response in 2018 (b_C = −0.18 ± 0.008). Inter-annual differences in b_C may be caused by differences in q, however due to the gaps in the time series, we attribute most the inter-annual differences to missing data, particularly when where different periods of the year excluded from the analyses (figure 2; figure S2).

Overall our b_C values are lower than those reported for 1st- to 6th-order streams (b_C ranging from −0.05 to 0) and larger rivers (b_C ranging from 0.02 to 0.24) throughout the USA (Liu and Raymond 2018). Low b_C values are indicative of dilution as a response to increasing q, which in mountain streams is certainly
facilitated by an acceleration of $k_{\text{CO}_2}$ that also increases with discharge (hence also with $q$) and related hydraulics. The $b_C$ values from our study streams are comparable to those reported from small boreal streams draining forested and peatland catchments ($b_C$ ranging from $-0.36$ to $-0.08$) (Wallin et al 2010). Wallin et al (2010) found more negative responses of CO$_2$ concentration to discharge in streams with lower pH and hence lower carbon buffering capacity. We did not find a similar trend, possibly also because the pH in our study streams was typically $>8$. Only the streams in the Valssorey catchment were transiently undersaturated in CO$_2$ with respect to the atmosphere. We tentatively attribute this to low dissolved inorganic carbon concentrations in these streams (2–3 times lower compared to the other catchments) and thus less potential for inorganic carbon buffering.

The overall low $b_C$ values reported here may also be linked to the sparse sources from where CO$_2$ may emanate. This notion is supported by the trend showing $b_C$ values decreasing with increasing altitude across both water years ($R^2 = 0.39$, $n = 9$, $P = 0.07$; VEL and VID were outliers and excluded from this analysis; VIU did not show a significant response in CO$_2$ concentration to $q$), which could be linked to decreasing vegetation coverage with altitude in those two catchments. This notion is supported by increasing $b_C$ values with increasing vegetation coverage ($R^2 = 0.44$, $n = 10$, $P = 0.05$; VID and FED were outliers and excluded from this analysis).

Near-chemostatic behavior can occur when CO$_2$ supply balances CO$_2$ export through evasion and downstream transport fluxes. We attribute the annual near-chemostatis observed in some of our streams to substantial delivery of CO$_2$ via groundwater. In fact, groundwater has been shown to be important for the transport and related hydraulics of CO$_2$ (Wallin et al 2010) found more negative responses of CO$_2$ concentration to discharge in streams with lower pH and hence lower carbon buffering capacity. We did not find a similar trend, possibly also because the pH in our study streams was typically $>8$. Only the streams in the Valssorey catchment were transiently undersaturated in CO$_2$ with respect to the atmosphere. We tentatively attribute this to low dissolved inorganic carbon concentrations in these streams (2–3 times lower compared to the other catchments) and thus less potential for inorganic carbon buffering.

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Near-chemostatic behavior can occur when CO$_2$ supply balances CO$_2$ export through evasion and downstream transport fluxes. We attribute the annual near-chemostatis observed in some of our streams to substantial delivery of CO$_2$ via groundwater. In fact, groundwater has been shown to be important for the CO$_2$ dynamics in the streams in the Vallon de Nant catchment (RIC, AND, ANU) (Horganby et al 2019). Beyond our mountain streams, groundwater is now being increasingly recognized to drive CO$_2$ concentration and fluxes in various headwater streams (Duvert et al 2018, Lupon et al 2019). Because of the inherent link between gas exchange velocity and discharge, we found positive responses in $k_{\text{CO}_2}$ to $q$ (100%, $P < 0.05$) and $F_{\text{CO}_2}$ to increasing $q$ (53%, $P < 0.05$) (Table S2). Of the 24 $b_p$ only 2 were from non-significant relationships (from VAD 2017 and PEU 2018). The median $b_C$ value for the 22 significant $F_{\text{CO}_2}$ - $q$ relationships was $-0.004$, ranging from $-0.20$ to $0.32$ across the streams (table S2). Liu and Raymond (2018) found, in their systematic survey on US streams and rivers, the highest $b_C$ values ($0.23$–$0.31$) in small streams. We relate the different relationships observed in their study and ours to the overall low CO$_2$ concentrations in our mountain streams. In fact, low streamwater CO$_2$ concentration reduces the CO$_2$ gradient between the streamwater and the atmosphere, and hence $F_{\text{CO}_2}$. This is further supported by the positive relationship between $b_p$ and vegetation coverage ($n = 11$, $R^2 = 0.33$, $P = 0.05$; VID excluded as outlier) for the same reasons as discussed above.

3.4. Short-time responsiveness of CO$_2$ to specific discharge and CO$_2$ sources

While most study streams exhibited dilution to quasichemostasis behavior for CO$_2$ concentration on an annual basis, we also detected windows with positive $b_C$ values in five of our study streams (VAD: $b_C = 0.55 \pm 0.05$, $n = 73$, $R^2 = 0.59$; VAU: $b_C = 0.32 \pm 0.03$, $n = 269$, $R^2 = 0.37$; FED: $b_C = 0.20 \pm 0.01$, $n = 865$, $R^2 = 0.27$; AND: $b_C = 0.10 \pm 0.002$, $n = 2592$, $R^2 = 0.57$; ANU: $b_C = 0.13 \pm 0.002$, $n = 2304$, $R^2 = 0.76$; all with $P < 0.05$) that were typically associated with the freshet during spring snowmelt (figure S2). This short-term behavior indicates that these streams received substantial CO$_2$ deliveries during specific periods.

The notion of increased CO$_2$ deliveries during freshet (i.e. the onset of snowmelt), is further supported by our stable isotope analyses. Across all streams, stable isotope analysis consistently revealed depleted CO$_2$ compositions ($\delta^{13}$C-CO$_2$) in spring (April: median $\delta^{13}$C-CO$_2$: $-15.81\%$; March: $-15.47\%$; May: $-14.39\%$) but more enriched composition in August ($-11.73\%$) and later in February ($-11.83\%$) and January ($-11.90\%$) (streams were not accessible in December) (figure 3). These isotopic compositions indicate that during the spring freshet, there are proportionally less contributions of CO$_2$ from geogenic sources (i.e. more enriched compositions). Moreover, it suggests CO$_2$ from soil respiration as a source to the streams during the spring freshet, coinciding with the hydrological activation of the headwater network. In fact, respiratory CO$_2$ ultimately from the heterotrophic breakdown of organic matter typically has isotopic compositions ranging from $-34$ to $-24\%$ (Wang et al 1998) and is hence more depleted than atmospheric CO$_2$ and CO$_2$ with carbonate origin (Clark and Fritz 1997). Our observation of a respiratory CO$_2$ pulse during the freshet is in agreement with previous observations from high-altitude and high-latitude catchments (e.g. Dinsmore and Billett 2008; Dinsmore et al 2013), and further corroborates the notion of microbial activity underneath the snow cover leading to CO$_2$ accumulation (Mast et al 1998). Increasing hydrological connectivity during snowmelt facilitates the transportation of this CO$_2$ via shallow groundwater flow paths to the streams (Doctor et al 2008). The delivery of CO$_2$ from the terrestrial environment to streams is analogous to the DOC flushing during snowmelt (sensu Boyer et al 2000), and as it has been observed in our study streams as well (Boix Canadell et al 2019). This further supports the relevance of this short window for carbon fluxes at the scale of high-altitude catchments.

Our findings reveal the window of the freshet as potentially important for carbon fluxes in high-altitude catchments. During freshet, the $F_{\text{CO}_2}$ increased rapidly over a short time period. For instance, during
5 d of freshet in 2017, $F_{\text{CO}_2}$ at FED increased from 1.5 g C m$^{-2}$ d$^{-1}$ (11 May, 2017) to 2.2 g C m$^{-2}$ d$^{-1}$ (16 May, 2017). Similarly, during 16 days of freshet in 2018, $F_{\text{CO}_2}$ at ANU increased from 3.0 g C m$^{-2}$ d$^{-1}$ (1 April, 2018) to 8.0 g C m$^{-2}$ d$^{-1}$ (16 April, 2018).

3.5. CO$_2$ dynamics across temporal scales

This study reveals different responsiveness of CO$_2$ concentration and fluxes to $q$ depending on the temporal scale. In line with our conceptual framework (figure 1), we found a clear transition of the CO$_2$ dynamics and its potential drivers from an annual to the event-driven (i.e. freshet) scale (figure 4). On an annual basis, the relationship between $b_F$ and $b_C$ was largely constrained to the domain where CO$_2$ dilution governs the evasion fluxes (see also figure 1). This was particularly true for high-elevation catchments. During the freshet (onset of the snowmelt period) the CO$_2$ source limitation became relieved, which resulted in a higher $F_{\text{CO}_2}$ responsiveness to specific discharge.
carbon stocks. The latter have higher potential to generate CO₂ from soil respiration, for instance, that can be delivered to the streams. The freshet is a window where the CO₂ source limitation becomes transiently relieved enabling an increase in F_CO₂. This is furthermore facilitated by an accelerated gas exchange due to increasing q.

4. Conclusions

Across the 12 studied mountain streams, we found varying and temporally dynamic responsiveness of CO₂ and F_CO₂ to q. Streamwater CO₂ dilution, likely a consequence of source limitation, was the general response to increasing specific discharge on an annual basis. The spring freshet was found to be a window where source limitation was relieved and CO₂ from soil respiration could be flushed to the streams. This window is potentially relevant for carbon fluxes at the catchment scale as it is certainly susceptible to snow dynamics owing to climate change in the Alps.

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Competing interest

The authors declare that they have no conflict of interest.

Data availability

The data presented can be found at DOI: 10.6084/m9.figshare.10293458.

Author contributions

ÅH, TJB and LGG planned and designed the research; NE acquired, managed and curated the data; ÅH performed the stable isotope analyses and other laboratory work and analyzed the data with support from LGG; ÅH wrote a first version of the manuscript; T J B contributed to the final version together with LGG and NE.

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