Aquatic-Terrestrial Linkages Control Metabolism and Carbon Dynamics in a Mid-Sized, Urban Stream Influenced by Snowmelt

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Abstract Freshwater streams can exchange nutrients and carbon with the surrounding terrestrial environment through various mechanisms including physical erosion, flooding, leaf drop, and snowmelt. These aquatic-terrestrial interactions are crucial in carbon mobilization, transformation, ecosystem productivity, and have important implications for the role of freshwater ecosystems in the global carbon budget. We utilized high-frequency oxygen, temperature, and carbon dioxide (CO2) data to infer watershed connectivity in Boulder Creek, a mid-sized (1160 km2) watershed located in Colorado, USA. Daily modeled gross primary production (GPP), ecosystem respiration (ER), net ecosystem production (NEP), and reaeration coefficients (K_{em}) were paired with high-frequency, in-situ dissolved CO2 data to characterize changes in metabolic regime and carbon flux on a stream influenced by seasonal snowmelt. GPP and ER were correlated (ρ = −0.72, p < 0.001) during the non-snowmelt period and NEP was frequently negative. Mean F_{CO2} during the non-snowmelt period was approximately 302 (±171) mmol C m⁻² d⁻¹ and was primarily supported by watershed CO2 inputs. During snowmelt, GPP and ER were not significantly correlated (ρ = −0.22, p = 0.05), and mean NEP was significantly more negative than during non-snowmelt. Watershed connectivity was higher during snowmelt, as evidenced by significantly higher F_{CO2} (843 ± 338 mmol C m⁻² d⁻¹) and greater allochthonous CO2 inputs than during non-snowmelt periods, emphasizing the effects of seasonal differences in aquatic-terrestrial linkages in this stream. We suggest that our understanding of watershed carbon budgets is subject to temporal dynamics which control the degree of connectivity between terrestrial and aquatic ecosystems.

Plain Language Summary Freshwater streams can exchange nutrients and carbon with the surrounding terrestrial environment through various mechanisms including physical erosion, flooding, leaf drop, and snowmelt. The dynamic nature of nutrient and carbon exchange between aquatic and terrestrial environments is important to understand because aquatic ecosystems have the capability of releasing terrestrially-bound carbon on a rapid timescale. This has implications for the global carbon cycle, a direct factor when considering climate change. We used dissolved gas measurements to model ecosystem parameters in order to characterize variations in nutrient and carbon dynamics in a mid-sized stream that receives seasonal snowmelt. We observed a seasonal increase in carbon dioxide flux in the stream and a distinct shift in aquatic metabolic processes directly correlated with annual snowmelt, an event that significantly increases streamflow. Long-term monitoring is needed because seasonality of hydrology alters the relationship between terrestrial productivity and aquatic ecosystem processes, which in turn can affect water quality and the global carbon budget.

1. Introduction

Freshwater streams exchange nutrients and carbon with the surrounding terrestrial environment through various mechanisms including physical erosion, flooding, leaf drop, and snowmelt. These interactions are important in governing the transport of carbon and nutrients, which in turn control trophic status and the metabolic functioning of aquatic ecosystems. The linkage between aquatic and terrestrial environments can be better understood and quantified through modeled metabolism rates. Metabolism is an encompassing term for the biological reactions of gross primary production (GPP), ecosystem respiration (ER), and their sum-net ecosystem production (NEP = GPP + ER, where ER is negative by convention). NEP indicates the net balance between biomass production and mineralization (Odum, 1956). Positive NEP suggests sustained...
biomass (organic matter) accumulation, while negative NEP, also called “net heterotrophy,” indicates net mineralization which is fueled by inputs of allochthonous organic carbon (OC) from the surrounding watershed. Despite the geographic and seasonal variability associated with stream metabolic processes, net heterotrophy is a common condition and emphasizes the importance of terrestrial OC in influencing stream biological processes (Battin et al., 2009; Bernhardt et al., 2018; Hall et al., 2016).

Seasonal or irregular disturbances to the hydrologic regime, such as annual fluxes of snowmelt, can affect stream metabolism by mobilizing OC into aquatic ecosystems and by physically disrupting primary producers (Palmer & Ruhi, 2019). For example, ER and GPP can be significantly reduced due to mobilization of the streambed after major flooding events in urban stream corridors (Reisinger et al., 2017; Smith & Kaushal, 2015). However, the response of stream metabolism to hydrologic disturbance is variable. For example, high flows can increase inputs of territorially derived OC (Boyer et al., 1997), which can maintain elevated ER by providing an exogenous carbon source to stream heterotrophs (Demars, 2019). GPP and ER may also increase rather than decrease in response to snowmelt-driven flow increases because these events are associated with less scour and potentially increases in light and nutrient availability (Ulseth et al., 2018). High-flow events can also enhance CO₂ flux (Fₐ₉) from surface waters by the combined effects of increased OC mobilization, which can increase stream heterotrophy, and direct inputs of inorganic carbon of terrestrial origin (Demars, 2019).

The influence of terrestrial inputs on stream Fₐ₉ is related to stream size and discharge, which creates spatial variability and influences the magnitude of Fₐ₉ from streams (Hotchkiss et al., 2015). Smaller, low order, streams have relatively high loading of terrestrial carbon, both OC and CO₂, which significantly influences the carbon and metabolic dynamics of the stream, resulting in a high rate of Fₐ₉. In contrast, the relative influence of terrestrial carbon on larger rivers, or high order streams, is diminished, and CO₂ dynamics are governed to a larger degree by processes internal to the stream, such as NEP (Hotchkiss et al., 2015). However, the spatial structure of stream carbon biogeochemistry and its relation to metabolism is likely to be temporally variable due to differences in the degree of watershed connectivity. Therefore, expanded understanding of temporal and spatial controls on stream Fₐ₉ and its relation to internal and external controls on the watershed is needed, as it can ultimately impact water quality and the global carbon budget (Butman & Raymond, 2011; Butman et al., 2016).

New tools, especially relatively inexpensive and reliable environmental sensors and modeling approaches, allow for long-term and expanded insights into metabolic rates, carbon fluxes, temporal stream dynamics and drivers (Battin et al., 2009; Bernhardt et al., 2018; Smith & Kaushal, 2015). The expanding prevalence of high-frequency CO₂ observations allows more detailed analysis of Fₐ₉. Pairing these observations with dissolved oxygen (DO) also allows the estimation of the gas exchange velocity from metabolism model estimates. These estimates can be made on a daily timescale, which contrasts with approaches that rely on periodic direct measurements of Fₐ₉ from stream surfaces (Striegl et al., 2012) or broad syntheses that couple calculated pCO₂ with statistical representations of the gas exchange velocity (Battin et al., 2009; Butman & Raymond, 2011). Current Fₐ₉ estimates from fresh waterbodies are based on relatively sparse data and typically do not account for diel changes in dissolved CO₂ concentrations (Battin et al., 2008; Butman & Raymond, 2011; Butman et al., 2016; Stets et al., 2017). Therefore, a greater understanding of the effects of seasonal dynamic hydrology on terrestrial productivity and aquatic ecosystem processes can be gained by incorporating updated CO₂ observations and modeling techniques to include high-frequency Fₐ₉ estimates.

We used high-frequency DO and CO₂ observations to gain expanded insights into the seasonal patterns of stream metabolism and Fₐ₉ and the implications for watershed connectivity in a snowmelt-dominated stream. We sought to answer the questions: How does the relationship between GPP and ER, including the rate of NEP, vary between snowmelt and nonsnowmelt seasons? Does the magnitude of Fₐ₉ vary seasonally? How much of the Fₐ₉ can be attributed to stream net heterotrophy (negative NEP) and does this vary seasonally? High-frequency sensor data, including DO, pCO₂, light, and temperature, coupled with stream discharge data, were collected over a 2-year period in Boulder Creek, Colorado, USA. Daily modeled metabolism rates and high-frequency Fₐ₉ estimates were crucial to identify seasonal changes in stream productivity and ultimately carbon transformation in the stream.
2. Materials and Methods

2.1. Site Overview

The Boulder Creek watershed is approximately 1,160 km² and is located on the eastern slope of the Rocky Mountains in Colorado (Figure 1). The headwaters originate at the continental divide and flow through the alpine, subalpine, montane, foothills, and plains ecoregions. The upstream, mountainous part of the watershed is sparsely populated and primarily forested, whereas the lower plains region consists of urban and agricultural land use (Murphy, 2006). The study site was co-located with U.S. Geological Survey (USGS) stream-gaging station 06730200 (USGS, 2020), on Boulder Creek downstream of the city of Boulder (but upstream of the city’s wastewater treatment plant), at an elevation of 1,562 m above sea level with a 795 km² drainage area. Only 8% of the Boulder Creek Watershed upstream of the study site is developed (urban) land use, indicated with gray shading in Figure 1 (calculated using StreamStats). The area near the monitoring location is used recreationally for fishing, swimming, biking, and walking.

2.2. Discharge and Stream Depth

Seasonal and annual variations in stream discharge (Q) of Boulder Creek are dominated by snowmelt events and water management practices (Murphy et al., 2003). Snowmelt events are defined by seasonal increases in Q caused by rapidly melting snow in the warmer spring and summer months, and therefore were determined from the rate and timing of streamflow of Boulder Creek (Figure S1). The beginning of snowmelt is evident from a rapid, continuous rise in Q in the spring. The end of the snowmelt period was estimated from timing of a rapid decrease to a relatively constant Q at an upstream gaging station with fewer diversions (Colorado Division of Water Resources State Gage BOCOROCO near Orodell, CO). During the snowmelt season, melting alpine snowpack exceeds the holding capacity of reservoirs in the basin and exceeds the rate of diversions in the watershed (Murphy, 2006), which allows a stronger connection between the upper and lower parts of the basin. The snowmelt period (approximately April to July) is also the wettest time of the year in the lower part of the basin. For example, on average, half of the 50 cm of precipitation that Boulder receives annually occurs during the period between April and July (https://www.esrl.noaa.gov/psd/boulder/Boulder.mm.precip.html), as snow, rain, or mixed precipitation.
Water management practices that alter the flow regime of Boulder Creek include reservoirs, diversions into and out of the watershed, and wastewater effluent inputs. A trans-basin supply canal located about 800 m upstream of the study site (referred to here as the “supply canal”; Figure 1) delivers water diverted from the western slope of the Rocky Mountains to Boulder Creek from April to October (Murphy, 2006), and contributed between 0% and 95% of the base flow in Boulder Creek during the study period (Figure S2). Discharge data for the supply canal (Northern Water, https://www.northernwater.org) minus a diversion from the canal was used to determine actual streamflow contributions to Boulder Creek. This input could have affected the DO and dissolved CO₂ dynamics at the study location; therefore, we limited the metabolism analysis to days when this diversion contributed less than 25% of the total flow of Boulder Creek (Figure S2). Overall, 110 days of DO data and 88 days of pCO₂ data were removed from the analysis due to >25% of Boulder Creek streamflow originating from the canal.

Stream discharge measurements for Boulder Creek at 75th Street (USGS stream-gaging station 06730200) were obtained from the USGS National Water Information System (USGS, 2020). Mean reach depth was measured in November of 2016 and was related to the gage height, which is reported at 15-min intervals. Mean reach depth was estimated from cross-sections performed every 10 m over the calculated DO reach length, determined as 3v/K₆₀₀ where K₆₀₀ is the reaeration coefficient and v is average velocity in m d⁻¹ (Chapra & DiToro, 1991). After several months of data collection in which initial estimates of GPP, ER, and K₆₀₀ were obtained (not shown), the model was re-run for the entire data collection period after correcting to the new mean depth estimate.

2.3. Dissolved Gases, Temperature, and Light Measurements

Temperature, DO, dissolved CO₂, and light intensity measurements were collected from Boulder Creek upstream of 75th Street from June 2016 to May 2018. Temperature and DO measurements were collected at 10-min intervals using a submersible miniDOT dissolved oxygen logger manufactured by Precision Measurement Engineering (Vista, CA, USA). The factory calibration for the miniDOT probes was internally validated and subsequently utilized for the first year of data collection. Precision Measurement Engineering ensured DO and temperature calibration to be within ±5% and 0.1°C, respectively. The second year of use, the miniDOT probes were calibrated using a membrane inlet mass spectrometer (MIMS; Hall et al., 2016). Calibration samples were collected by syphoning Boulder Creek water into a 12-mL glass exetainer in triplicate and preserving with 100 μL of 50% w/v zinc chloride, then carefully capping to ensure no air bubbles were present in the vial. Samples were stored at room temperature until analysis. Correction factors were calculated by converting the mass-32 peak obtained from the MIMS software into a DO concentration and comparing the value to the DO measurement in the stream when the sample was collected (adjusting for temperature and pressure; Kana et al., 1994). Calibration factors were assumed to be a linear offset and were between 0.06 and 0.73 mg L⁻¹ in year two of the study. The temperature sensor was factory calibrated and was assumed to maintain an error range of ±0.1°C throughout the experiment.

Dissolved CO₂ measurements were collected using a Vaisala GMT220 with a CO₂ concentration range of 0–10,000 ppm CO₂ (Vantaa, Finland). The probe was wrapped in high-porosity polytetrafluoroethylene (PTFE) sleeve (a gas-permeable, water-impermeable material) sealed with plasticized rubber to prevent water entry (Johnson et al., 2010). The probe was calibrated with 0, 390, 1051, 2024, 4020, and 6080 ppm certified CO₂ standards purchased from Airgas. The calibration curve related a known CO₂ concentration to a voltage output. The slope and offset generated by the standard curve were incorporated into the SEVolt command of the Campbell Scientific CR1000 code (Crawford et al., 2017). Dissolved CO₂ measurements were recorded using the Campbell Scientific CR1000 Measurement and Controller System with 1-h resolution. Raw CO₂ concentrations were adjusted for temperature and pressure and converted to mole fraction CO₂. The partial pressure of CO₂ in the aqueous phase (pCO₂) was calculated by multiplying the mole fraction by the barometric pressure in atmospheres. Barometric pressure was estimated to be 850 hPa for the entire study based on the elevation at the study site. We have found in previous intercomparisons of several CO₂ sensing/measurement methods that the Vaisala GMT220 probe performed well when compared to serum bottle, syringe equilibration, or carbonate system estimates (calculated from alkalinity, temperature, and pH) under a range of conditions. Stets et al. (2017) reported strong coherence between Vaisala CO₂
measurements and those of the syringe equilibration method (In a comparison done for another project, we found: Vaisala CO₂ (ppm) = 576 + 0.98(Serum CO₂), rsq = 0.97 (Stets et al., 2017).

Light intensity measurements were collected using an Onset HOBO Pendant Temperature/Light Data Logger (Cape Cod, MA, USA). The pendants were factory calibrated at the start of the experiment. According to manufacturer specifications, light measurements are relative readings and account for light waves between 500 and 1100 nm with ≥50% response. Modeled light was used instead of light measurements if: (1) stream depth was ≥1.59 m; (2) if an observation between 10:00 and 15:00 local time registered as zero; or, (3) if there were no observed light data due to equipment malfunction. Approximately 50% of the light data utilized in the metabolism model were modeled light. Light data were fit to a localized polynomial regression to minimize outliers.

All probes were attached to a steel fireplace grate and securely positioned in the thalweg of the streambed with rebar. All sensors were fully submerged for the duration of the study and were oriented downstream to prevent damage from large floating objects. The light sensor was oriented horizontal to the streambed. Sensors were maintained on a weekly basis during warmer months (approximately April-September), and biweekly basis during colder months (approximately October-March). Gaps in the final dataset are due to either sensor malfunction or exclusion of the data due to the supply canal providing >25% of streamflow to Boulder Creek at the study site.

2.4. The Metabolism Model

Stream metabolism was estimated using the R package streamMetabolizer (Appling et al., 2017). The model uses a hierarchical Bayesian approach to solve the equation:

\[ O_2_t = O_2_{t-1} + P_t + R_t - R_{O_2t} \]  \hspace{1cm} (1)

where \( O_2_t \), \( P_t \), \( R_t \), and \( F_{O_2t} \) represent DO concentration and volumetric expressions of gross photosynthesis, ER, GPP, and the change in \( O_2 \) across the air-water interface at time \( t \), respectively. \( R_t \) is negative by extension of \( ER \) being designated as negative. The model fits the volumetric parameters GPP, ER, and the reaeration coefficient \( K_{O_2} \) to reproduce the oxygen time series as closely as possible using an inverse modeling approach. \( R_t \) was related to ER as

\[ R_t = ER \cdot \frac{1}{z} \]  \hspace{1cm} (2)

where \( z \) represents the depth of the water column and \( R_t \) and \( ER \) are volumetric units.

\( P_t \) was related to GPP through \( z \) and photosynthetic photon flux density (PPFD) as

\[ P_t = GPP \cdot \frac{1}{z} \cdot \frac{\text{PPFD}_t}{\sum \text{PPFD}} \]  \hspace{1cm} (3)

where \( \text{PPFD}_t \) is the photosynthetic photon flux density at time \( t \), measured as light intensity, and \( \sum \text{PPFD} \) is the total light flux for a 24-h period. Because \( \sum \text{PPFD} \) is required to run the model, light data were handled such that days with complete observational records were used preferentially. On some days incomplete or unusable light data were collected due to instrument failure or extreme shading from sediment, detritus, or debris. In these cases, PPFD was calculated using geographic location and day of the year (Yard et al., 2005) and is a built-in function of streamMetabolizer (Appling et al., 2017).

We assumed a linear response of stream GPP to light in the metabolism model. Modeling experimentation showed that the linear light model was conceptually appropriate for a natural stream setting due to the bulk of metabolism occurring at the benthic surface, where photosynthetic saturation is less probable due to light stratification of the water column. We tested this assumption by running the model in both linear and saturated light configurations and superimposing the modeled and observed DO data. The linear light model yielded more precise DO estimates, especially on highly productive days where maximum DO concentrations exceeded 12 mg L⁻¹. In this system, the saturated light configuration underestimated the daily maximum dissolved oxygen concentration as much as 25% and in some extreme cases overestimated by 150%.

In addition to GPP and ER estimates, streamMetabolizer estimates the flux of \( O_2 \) across the air-water interface and is given by
where \( K_{O2} \) is the oxygen reaeration coefficient, \( O_{2A} \) is the \( O_2 \) concentration at equilibrium with the atmosphere, and \( O_2t \) is the observed \( O_2 \) concentration at time \( t \). \( K_{O2} \) was related to \( K_{600} \) using the temperature-dependent Schmidt number (Jähne et al., 1987). \( O_{2A} \) was calculated for each time interval \( (t) \) based on temperature and barometric pressure.

Parameter values and uncertainties were obtained using Markov Chain Monte Carlo (MCMC) including both process and observation error, which helps to guard against overfitting (Appling et al., 2018). Partial pooling was achieved by binning daily discharge values to constrain \( K_{O2} \). Prior estimates for GPP were set to 93 (±63) mmol C m\(^{-2}\) d\(^{-1}\) based on preparatory experiments estimating metabolic rates in Boulder Creek. Two thousand burn-in steps were run prior to model parameter value output collection. All model options were specified in streamMetabolizer using the specs function. Model estimates were converted from g \( O_2 \) m\(^{-2}\) d\(^{-1}\) to mmol C m\(^{-2}\) d\(^{-1}\) by assuming a one-to-one molar ratio between \( O_2 \) and C (Stets et al., 2017).

### 2.5. Calculations and Estimates of \( F_{CO2} \)

Values for \( pCO_2 \) were converted to concentration values using Henry’s law (Butler, 1982). \( F_{CO2} \) at time \( t \) \((F_{CO2t})\) was also estimated using the calculated \( CO_2 \) concentrations and the \( K_{600} \) values produced through streamMetabolizer using the equation

\[
F_{CO2t} = k_{CO2} \bullet (CO_{2t} - CO_{2A})
\]

where \( k_{CO2} \) is the gas exchange velocity of \( CO_2 \), \( CO_{2A} \) is the concentration of \( CO_2 \) in equilibrium with the atmosphere at time \( t \), and \( CO_{2t} \) is the observed \( CO_2 \) concentration at time \( t \). \( k_{CO2} \) was calculated from \( K_{600} \) using stream depth \((z)\) and the temperature-dependent Schmidt number (Jähne et al., 1987; Striegl et al., 2012). \( CO_{2A} \) was calculated from Henry’s law constant by assuming that atmospheric \( CO_2 \) was 390 ppm and correcting for barometric pressure. Hourly \( F_{CO2} \) estimates were integrated to produce daily estimates of \( F_{CO2} \). By convention, positive values of \( F_{CO2} \) indicate a mass loss of \( CO_2 \) from the stream to the atmosphere.

Pairing daily, modeled \( K_{600} \) with \( pCO_2 \) sensor readings to estimate \( F_{CO2} \) minimizes artifacts associated with the carbonate buffering system, such as diel lags in \( CO_2 \) concentration and flux (Stets et al., 2017), and expanded the temporal scale such that \( F_{CO2} \) could be reasonably compared to daily NEP to determine the contribution of NEP to \( F_{CO2} \) in Boulder Creek.

### 3. Results

#### 3.1. Hydrologic Regime

The study period encompassed one full snowmelt period and two partial snowmelt periods (Figure 2). Mean \( Q \) during both of the snowmelt periods was approximately eight times higher than during the non-snowmelt periods, with over half of annual discharge (54%) occurring in May and June (Figure 2). Peak discharge in 2016, 2017, and 2018 was 23.8, 23.5, and 24.7 m\(^3\) s\(^{-1}\), respectively, compared to 34.3 and 41.3 m\(^3\) s\(^{-1}\) in 2014 and 2015 respectively (Figure 2). A statistical summary of \( Q \) for the full study can be found in Table 1.

#### 3.2. DO and \( pCO_2 \) Dynamics

The DO record covers 518 days out of the 723 total days of the study. Of these 518 days, 110 days (21%) were removed from the analysis due to >25% of streamflow originating from the supply canal and 53 days (10%) contained insufficient data for the metabolism model and were dropped from analysis. Overall, 355 days (49% of the study period) are represented in the final metabolism analysis (Figure 3a). The relationship between observed DO and \( pCO_2 \) can be found in Figure S3.
DO concentrations exhibited diel changes (Figure 3b), with the highest DO concentrations typically observed just after solar noon and the lowest DO concentrations observed before sunrise. Mean DO concentration across the entire study was approximately 9.70 (±2.27) mg L⁻¹. Monthly, mean DO concentration was highest in January (10.9 ± 1.54 mg L⁻¹) and lowest in June (8.22 ± 0.908 mg L⁻¹). Mean DO concentration during the snowmelt and non-snowmelt periods were 8.39 (±0.900) mg L⁻¹ and 10.1 (±2.39) mg L⁻¹, respectively (not shown).

The record for pCO₂ covers 209 days out of the 723 total days of the study (29%). However, we removed 88 days from the analysis due to (1) the supply canal contributing >25% of baseflow to Boulder Creek at the study site and (2) non-overlapping modeled metabolism rates and pCO₂ data. The final analysis contained 121 days of pCO₂ data (Figure 3c).

### Table 1

A Statistical Summary of Various Parameters Pertinent to This Study (Discharge (Q), Water Temperature, Water Depth, Dissolved Oxygen (DO), Reaeration Coefficient (K₆₀₀), Net Ecosystem Production (NEP), Gross Primary Production (GPP), Ecosystem Respiration (ER), Dissolved Carbon Dioxide (pCO₂), and Carbon Dioxide Flux (FCO₂))

| Parameter | Units | 5th percentile | 95th percentile | Average | Standard deviation |
|-----------|-------|----------------|----------------|---------|--------------------|
| Q         | m³ s⁻¹ | 0.259          | 11.1           | 2.35    | 3.38               |
| Water temperature | °C | 0.099 | 15.2 | 7.54 | 5.11 |
| Water depth | m | 0.263 | 1.01 | 0.492 | 0.231 |
| DO        | mg L⁻¹ | 5.90          | 14.2           | 9.70    | 2.27               |
| K₆₀₀      | d⁻¹    | 7.70          | 36.10          | 16.4    | 8.28               |
| NEP       | mmol C m⁻² d⁻¹ | −371 | 115 | −89.8 | 137 |
| GPP       | mmol C m⁻² d⁻¹ | 34.1 | 382 | 159 | 128 |
| ER        | mmol C m⁻² d⁻¹ | −561 | −79.0 | −248 | 143 |
| pCO₂      | ppm    | 644           | 2380           | 1500    | 531                |
| FCO₂      | mmol C m⁻² d⁻¹ | 137 | 1160 | 506 | 363 |

Note. Values account for observations across the entire study.
Diel patterns in $pCO_2$ persisted in both snowmelt and non-snowmelt conditions, with less prominent fluctuations observed in the spring and larger fluctuations in the fall (Figure 3d). Mean $pCO_2$ across the entire study was approximately 1,500 (±531) ppm (Figure 3c). Monthly mean $pCO_2$ was highest in October (1,690 ± 680 ppm) and lowest in June (1,410 ± 465 ppm). Mean $pCO_2$ was slightly lower during snowmelt (1,480 ± 431 ppm) than in the non-snowmelt (1,580 ± 613 ppm) period. Carbon dioxide flux ($F_{CO_2}$) was also estimated as the product of observed CO$_2$ concentrations and $K_{600}$ obtained from the metabolism model. Mean $F_{CO_2}$ across the entire study was 506 (±363) mmol C m$^{-2}$ d$^{-1}$ (Figure 7b). Mean $F_{CO_2}$ during the snowmelt period (843 ± 338 mmol C m$^{-2}$ d$^{-1}$) was almost three times higher than mean $F_{CO_2}$ during the non-snowmelt period (302 ± 171 mmol C m$^{-2}$ d$^{-1}$).

### 3.3. Metabolism Model Estimates: GPP, ER, NEP, and $K_{600}$

Across both years of the study, January had the lowest mean rate in ER (157 mmol C m$^{-2}$ d$^{-1}$), while May had the highest mean rate in ER (−458 mmol C m$^{-2}$ d$^{-1}$; Figures 4a and 4b). The maximum (i.e., most negative) and minimum (i.e., least negative) daily ER estimates were observed in December and February, respectively. Mean ER was −469 (±135) mmol C m$^{-2}$ d$^{-1}$ during the snowmelt period and −239 (±92.2) mmol C m$^{-2}$ d$^{-1}$ during the non-snowmelt period (not shown). The standard deviation on daily ER estimates averaged 144 mmol C m$^{-2}$ d$^{-1}$ and had highest absolute value when the rate of ER was high but was a higher proportion of ER when it was closer to zero.

Rates of GPP were high, but large variations were observed between days and seasons. Across both years of the study, June had the highest mean GPP, while December had the lowest mean GPP (Figures 4c and 4d).
Figure 4. (a, c, e, g) Modeled monthly estimates of ER, GPP, NEP, and $K_{600}$ respectively, in Boulder Creek at 75th Street for the period June 2016 through May 2018. Hollow squares represent the mean metabolism rate for each month. The black dashed line represents the mean rate across the entire study. Blue numbers indicate the number of days across the 2-year study with a complete record (where a complete record is equal to 144 observations per day at 10-min intervals). (b, d, f, h) A time series of daily, modeled estimates for ER, GPP, and NEP, and $K_{600}$ respectively. Pink shading indicates periods when the supply canal contributed >25% of flow to Boulder Creek at the study site and were omitted from all analyses. Blue shading represents snowmelt periods. Gray shading represents standard error.
The maximum and minimum daily GPP calculations were observed in June (802 mmol C m\(^{-2}\) d\(^{-1}\)) and December (167 mmol C m\(^{-2}\) d\(^{-1}\)), respectively. Mean GPP was 214 (±154) mmol C m\(^{-2}\) d\(^{-1}\) during the snowmelt period and 143 (±117) mmol C m\(^{-2}\) d\(^{-1}\) during the non-snowmelt period (not shown). Throughout the study period, the standard error on the daily GPP averaged 128 mmol C m\(^{-2}\) d\(^{-1}\). Similar to the other metabolic parameters, the absolute uncertainty on GPP was larger when GPP was larger, but values close to zero had higher relative uncertainties.

Mean NEP was negative for all months with available metabolism data (nine months), indicating net heterotrophy in Boulder Creek throughout the study (Figures 4e and 4f). The most negative monthly mean NEP was observed in December, estimated at −773 (±127) mmol C m\(^{-2}\) d\(^{-1}\). Mean NEP during the snowmelt season was almost five times higher than mean NEP during the non-snowmelt season, with NEP during the snowmelt period averaging −239 (±161) mmol C m\(^{-2}\) d\(^{-1}\) and −49.0 (±95.4) mmol C m\(^{-2}\) d\(^{-1}\) during the nonsnowmelt period.

The metabolism model produced \(K_{600}\) values that ranged from 1.33 to 43.7 days\(^{-1}\) and averaged 16.4 days\(^{-1}\) over the entire duration of the study (Table 1; Figures 4g and 4h). The mean for \(K_{600}\) during snowmelt (23.5 days\(^{-1}\)) was almost double of \(K_{600}\) estimations in the non-snowmelt (14.3 days\(^{-1}\)) seasons. Standard errors in daily \(K_{600}\) estimates averaged ±8.25 days\(^{-1}\). Absolute uncertainty (standard deviation) was highest when \(K_{600}\) was also high, but was proportionately higher when \(K_{600}\) was low, sometimes exceeding 70% of the best \(K_{600}\) estimate.

Metabolism models can suffer from equifinality, a lack of uniqueness in parameter value estimates (Appling et al., 2018). The correlation between ER and \(K_{600}\) was moderate for the non-snowmelt season (\(r = −0.31, p ≪ 0.01\)) and was higher in the snowmelt season (\(r = −0.76, p ≪ 0.01\)). In the complete dataset the correlation was also moderate (\(r = −0.55, p ≪ 0.01\)) but showed significant scatter (Figure S4). So, despite the significant \(p\)-values, we believe the model provided interpretable results about metabolic relationships in Boulder Creek (Figure S4).

### 3.3.1. ER Versus GPP

Examining the relationship between GPP and ER provides insight into the metabolic regime of streams and can simplify expression of the response of stream biological communities to multiple drivers (Bernhardt et al., 2018). When GPP is equal to ER (depicted by the solid black line in Figure 5a), the supply of OC...
produced via GPP is balanced by OC consumption by ER. A majority (77%) of the ER and GPP estimates are below this line, implicating additional sources of OC that supports ER (i.e., net heterotrophy). The relationship between GPP and ER during this study in Boulder Creek was weaker in the snowmelt period than in the non-snowmelt period. GPP and ER were negatively correlated during the snowmelt ($\rho = -0.22$, $p = 0.05$) period and non-snowmelt ($\rho = -0.72$, $p < 0.001$) period (Figures 4, S5, and S6). The metabolic regime during the non-snowmelt period covered a wide range of GPP (3.83–802 mmol C m$^{-2}$ d$^{-1}$), with mean GPP being 214 (±154 mmol C m$^{-2}$ d$^{-1}$) during snowmelt and 143 (±143 mmol C m$^{-2}$ d$^{-1}$) during the non-snowmelt period. The metabolic regime during the snowmelt period exhibited a narrower range of ER (−714 to −161 mmol C m$^{-2}$ d$^{-1}$) than the non-snowmelt period (−840 to −10.3 mmol C m$^{-2}$ d$^{-1}$; Figure 5c).

3.4. $F_{CO_2}$ and NEP

Most streams are net sources of CO$_2$ to the atmosphere, a phenomenon that can be caused by net heterotrophy or direct inputs of CO$_2$ from the watershed. Boulder Creek was no exception, with pCO$_2$ values above atmospheric equilibrium for all sensor observations and average $F_{CO_2}$ being positive in all months (Figure 3). Carbon dioxide flux ($F_{CO_2}$) was relatively high (97.8–1,340 mmol C m$^{-2}$ d$^{-1}$) with the highest $F_{CO_2}$ observed during the snowmelt period.

The relationship between $F_{CO_2}$ and NEP gives insight into the sources of CO$_2$ supporting $F_{CO_2}$ in Boulder Creek. A negative, one-to-one relationship (depicted by the solid black line in Figure 6a) between $F_{CO_2}$ and NEP suggests that net heterotrophy is the major source of excess CO$_2$ with little direct input of CO$_2$ from the watershed. Points above this line occur when the watershed contributes CO$_2$ to the stream which is then exchanged with the atmosphere. During the study period, a majority (99%) of $F_{CO_2}$ and NEP estimates were above the $y = x$ line, indicating that $F_{CO_2}$ is supported by a mixture of CO$_2$ produced through net heterotrophy in addition to CO$_2$ inputs from the watershed (e.g., terrestrial soils; Figure 6). Additionally, a strong negative correlation existed between $F_{CO_2}$ and NEP during snowmelt ($\rho = -0.62$, $p < 0.001$). An estimate of the percent contribution of watershed inputs of CO$_2$ to overall $F_{CO_2}$ ($W_{CO_2}$) can be made using the equation $W_{CO_2} = (100\% \times (1 - (\text{NEP}/F_{CO_2})))$. Watershed inputs were important in both snowmelt and non-snowmelt season, averaging 65% of the total CO$_2$ flux across the entire study. No significant difference was observed between the snowmelt (69%) and non-snowmelt seasons (63%; $p = 0.59$).
4. Discussion

4.1. The Importance of Allochthonous Carbon in Boulder Creek

As observed in many other systems, day-to-day variation in stream metabolic rates was wide, with GPP ranging one order of magnitude and ER ranging nearly one order of magnitude (Table 1; Bernhardt et al., 2018; Demars, 2019; Hall et al., 2016; Hoellein et al., 2013). We observed wide variability in the daily estimated metabolic parameters, with coefficient of variation (standard deviation divided by the mean) of GPP, ER, and $K_{600}$ being 81%, 58%, and 50%, respectively, over the course of the study period. Rates of GPP in Boulder Creek were high throughout the study, with the daily average GPP in Boulder Creek, 159 mmol C m$^{-2}$ d$^{-1}$, exceeding the average GPP for highly productive “summer peak” streams, 70 mmol C m$^{-2}$ d$^{-1}$ (Savoy et al., 2019).

We attribute these high, year-round GPP values to the hydrography of Boulder Creek at the study site. The study site exists in a hydrologically stable environment (due to water management practices) with relatively steady streamflow outside of snowmelt. This promotes the establishment of hardy primary producer communities that can metabolize year-round, even in the winter months when portions of the stream are ice-covered. Additionally, the upstream metabolic footprint of the study site and the study site itself lack a robust tree canopy cover, thereby increasing incident light to the streambed and increasing primary productivity (Bernhardt et al., 2018).
This study showed a reduction in correlation between GPP and ER in the snowmelt versus non-snowmelt season (Figures S5 and S6). Although net heterotrophy in streams is common in the literature (Battin et al., 2008; Savoy et al., 2019), some studies indicate high variability and low correlation between GPP and ER in streams (Bernot et al., 2010; Hoellein et al., 2013). For this particular study, the decoupling of GPP and ER, combined with high productivity, points to allochthonous OC fueling metabolism in Boulder Creek. Urbanization in the lower Boulder Creek watershed could be responsible for this decoupling due to consistent inputs of highly biodegradable OC (Table S1; Hosen et al., 2014). High biodegradability of allochthonous carbon would unlink GPP and ER by providing OC to heterotrophic bacteria through watershed inputs as opposed to GPP byproducts. Remineralization of urban, allochthonous carbon inputs (i.e., autochthonous carbon) at the study site is unlikely because almost all of the developed land upstream of the wastewater treatment plant with the exception of the snowmelt season (Murphy et al., 2003, p. 128).

ER was enhanced during the snowmelt period (Figure 5c). The enhancement of ER during snowmelt could arise from greater mobilization of OC into the stream channel or hydrologic and biogeochemical activation of adjacent floodways and riparian areas. Although DOC and TOC concentrations are low upstream of the wastewater discharges in Boulder Creek (<3 mg C L⁻¹), higher concentrations occur during snowmelt (see Chapter 5 in Murphy et al., 2003), indicating enhanced resources for heterotrophic mineralization during the snowmelt period. Additionally, DOC grab samples collected during the study period (Table S1) show, on average, higher DOC toward the beginning of snowmelt season (4.53 mg L⁻¹, n = 3) versus the non-snowmelt season (3.20 mg L⁻¹, n = 11). High flow conditions can also inundate and activate riparian zones and wetlands adjacent to streams, thereby stimulating mineralization of stored organic matter (Jacinthe, 2015), resulting in potential export of low oxygen water from these areas. This may be interpreted as enhanced stream respiration in the metabolism model used in this study.

GPP varied throughout the study and was marginally higher during the snowmelt period (Figure 5b). The lack of reduction in GPP during increased stream discharge associated with snowmelt is similar to findings in other snowmelt-dominated streams (Ulseth et al., 2018). Increased stream discharge is believed to decrease GPP due to shading from greater water column depths and scour from sediment disturbance (O'Connor et al., 2012; Reisinger et al., 2017). However, the seasonal increases associated with snowmelt may differ, in that they can be associated with less scour or are of sufficient duration to allow re-establishment of primary producers under increased flow conditions (Ulseth et al., 2018). Spring snowmelt is also unique in that it is associated with increasing light and potentially higher nutrient inputs. These findings strengthen the concept that the ecosystem response to seasonally-driven increases in stream discharge are distinct from those caused by storms and lend support to the generality of this idea.

4.2. Seasonality of Carbon Cycling

A persistent question about stream ecosystem functioning and its relationship to $F_{\text{CO}_2}$ is the degree to which excess CO$_2$ arises from excess stream respiration (i.e., net heterotrophy) versus direct CO$_2$ inputs from groundwater, riparian zones, or soil. Conceptually, direct inputs of CO$_2$ are greatest in headwater streams, where connections to the watershed are the strongest, and decrease downstream (Hotchkiss et al., 2015; Marx et al., 2017). Our ability to pair NEP values with $F_{\text{CO}_2}$ for a large number of days ($n = 121$) enables a direct estimate of the relative contribution of NEP versus watershed inputs in sustaining $F_{\text{CO}_2}$ from Boulder Creek (Figure 6). A negative correlation between NEP and $F_{\text{CO}_2}$ was evident during the snowmelt season (Figure 6, $\rho = -0.62, p \ll 0.001$), which supports the hypothesis that stream metabolic processes have a seasonal relationship with carbon dynamics. The moderate correlation of $F_{\text{CO}_2}$ to NEP during snowmelt is indicative of allochthonous OC stimulating ER, which in turn increases $F_{\text{CO}_2}$. NEP and $F_{\text{CO}_2}$ were not significantly correlated during the non-snowmelt period ($\rho = -0.12, p = 0.28$); however, further knowledge about the controls on GPP, ER, and NEP in Boulder Creek, and especially their relationships to the processes controlling CO$_2$ flux, is needed to answer this question more fully.

Not only is the role of allochthonous OC evident in Boulder Creek through the negative relationship between NEP and $F_{\text{CO}_2}$ and the decoupling of GPP and ER, but there is also evidence of allochthonous CO$_2$...
permeating the stream in the $F_{\text{CO}_2}$ signal. Carbon dioxide flux was higher during the snowmelt period ($p < 0.001$), despite a lack of seasonal change in $p\text{CO}_2$ from the annual mean ($p = 0.56$; Figures 7a and 7b). $K_{600}$ was significantly higher during the snowmelt season ($p = 0.003$), and largely drove the increases in $F_{\text{CO}_2}$ between the seasons. Short turnover time of $\text{CO}_2$ in Boulder Creek (on the scale of hours) throughout the year is conducive to high turnover of $\text{CO}_2$, even during the snowmelt season when $\text{CO}_2$ storage is higher ($p < 0.001$; Figures 7c and 7d).

4.3. Insights Gained from $F_{\text{CO}_2}$ Estimates

Unusually high temporal resolution of $F_{\text{CO}_2}$ was achieved by combining the $K_{600}$ estimated from metabolism modeling with sensor-based $p\text{CO}_2$, which provided enhanced interpretability of the biogeochemical effects of seasonality in this snowmelt-dominated mid-sized stream. Seasonal differences were particularly evident in the pairing of NEP estimates with $F_{\text{CO}_2}$ estimates (Figure 7); however, the measured metabolic shift (significantly more negative NEP) during snowmelt did not translate to significant seasonal differences in NEP contribution to overall $F_{\text{CO}_2}$ in Boulder Creek. Despite this finding, the novel methodology of coupling modeled $K_{600}$ with high-frequency $p\text{CO}_2$ observations may elucidate and help to refine the view of $\text{CO}_2$ transport and cycling in other mid-sized watersheds.

4.4. Dynamic Aquatic-Terrestrial Linkages in the Carbon Cycle

Emerging concepts about the degree of connectivity between streams and their watersheds are often based on long-term average behavior over large spatial scales. Many have proposed that low-order, headwater streams have greater connection to the watershed resulting in more intense carbon fluxes, either as dissolved inorganic carbon, which can be emitted directly as $\text{CO}_2$, or as $OC$, which maintains elevated ER and encourages net heterotrophy (Butman & Raymond, 2011; Butman et al., 2016; Finlay, 2011; Hotchkiss et al., 2015; Marx et al., 2017). However, the present study emphasizes the varying degrees of aquatic-terrestrial linkages that can occur at a single station depending upon seasonal flow regime. Boulder Creek acted as a low order stream during the snowmelt period and a high order stream during the non-snowmelt period with respect to $\text{CO}_2$ flux. Carbon dioxide flux rates increased during the snowmelt period and were likely sustained by an increase in $K_{600}$ and supplemented with increased inorganic carbon from the watershed (Figure 6). Metabolism during the non-snowmelt period was reliant on allochthonous $OC$, and direct $\text{CO}_2$ inputs were decreased (Figures 5 and 6). Thus, the concept of the relative intensity of the processes governing stream carbon flux in headwaters versus downstream systems (Hotchkiss et al., 2015; Marx et al., 2017) is supported; however, a temporal component should also be considered, which would alter the proportion of $F_{\text{CO}_2}$ originating from headwater versus downstream systems within a watershed.

5. Conclusion

The seasonal signal shown here emphasizes the temporally dynamic nature of aquatic-terrestrial linkages, especially with respect to its influence on carbon biogeochemistry. GPP and ER were negatively correlated throughout this study, but less negative during the snowmelt period. This uncoupling of GPP and ER, along with high metabolic productivity year-round, suggests the importance of allochthonous sources of $OC$ to maintain stream GPP and ER. Higher $F_{\text{CO}_2}$ during the snowmelt season further highlights the prominence and importance of allochthonous carbon inputs in Boulder Creek. This seasonal shift directly impacts the global carbon cycle by providing a direct mechanism for terrestrial $OC$ to be metabolized to $\text{CO}_2$ and soil-bound $\text{CO}_2$ to flux into the atmosphere more readily than would otherwise occur without seasonal aquatic-terrestrial linkages. The pairing of modeled metabolism estimates with $F_{\text{CO}_2}$ estimates was key in deciphering seasonal differences in carbon dynamics and is a novel way of estimating $F_{\text{CO}_2}$ on a daily timescale. The temporally dynamic nature of carbon biogeochemistry suggests that longer-term, dedicated monitoring is needed to fully resolve the connectivity and contribution of streams to the terrestrial component of watersheds and the global carbon budget.
Data Availability Statement
The data generated for this publication are publicly available (https://doi.org/10.5066/P9A4FVZ4; Reed, 2021).

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