







RESEARCH ARTICLE

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Integrating Ecosystem Patch Contributions to Stream Corridor Carbon Dioxide and Methane Fluxes

Key Points:

- Carbon dioxide and methane concentrations and emissions were heterogeneous within streams, even over short distances
- The year-to-year difference in stream carbon dioxide emissions was greater than monthly variability
- The presence of vernal pools in the stream corridor elevated overall stream corridor carbon emissions

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Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract The heterogeneity of carbon dioxide (CO₂) and methane (CH₄) sources within and across watersheds presents a challenge to understanding the contributions of different ecosystem patch types to stream corridor and watershed carbon cycling. Changing hydrologic connections between corridor patches (e.g., streams, vernal pools, hillslopes) can influence stream corridor greenhouse gas emissions, but the spatiotemporal dynamics of emissions within and among corridor patches are not well-quantified. To identify patterns and sources of carbon emissions across stream corridors, we measured gas concentrations and fluxes over two summers at Coweeta Hydrologic Laboratory, NC. We sampled CO₂ and CH₄ along four stream channels (including flowing and dry reaches), adjacent vernal pools, and riparian hillslopes. Stream CO₂ and CH₄ emissions were spatially heterogeneous. All streams were sources of CO₂ to the atmosphere (median = 97.2 mmol m⁻²d⁻¹) but were sources or sinks of CH₄ depending on location (−0.19 to 4.57 mmol m⁻²d⁻¹). CO₂ emissions were lower during the drier of two sampling years but were stable from month to month in the drier summer. CO₂ and CH₄ emissions also varied by both corridor and patch type; the presence of a vernal pool in the corridor had the strongest impact on emissions. Vernal pool patches emitted more CO₂ and CH₄ (246 and 1.95 mmol m⁻²d⁻¹, respectively) than their adjacent streams. High resolution sampling of carbon fluxes from patches within and among stream corridors improves our understanding of the connections between terrestrial, riparian, and aquatic zones in a watershed and their contributions to overall catchment carbon emissions.

Plain Language Summary Freshwater ecosystems can be sizable sources of greenhouse gases to the atmosphere. Carbon dioxide and methane emissions from freshwaters can be very different depending on where they are measured in a watershed. As distinct areas near a stream become connected by water moving through the watershed, stream greenhouse gas emissions may change in response to new carbon inputs from these connections. We studied carbon emissions from four streams and their surrounding patches: temporary pools, hillslopes adjacent to streams, and dry beds in stream channels (when water flowed underground). All streams emitted carbon dioxide and some streams were sources of methane to the atmosphere during our summer measurements, but emission magnitudes for both gases varied within each patch. Temporary pools were an important source of both greenhouse gases and contributed to stream emissions when present. Carbon dioxide emissions were lower in the drier of the two measurement summers, while methane emissions were similar. Sampling from many patches within and surrounding a stream improves our understanding of landscape-scale carbon emissions.

1. Introduction

As water moves carbon through watersheds and across ecosystem boundaries, stream corridors collect and integrate landscape-scale signals of carbon cycling. Streams metabolize organic carbon and emit carbon dioxide (CO₂) and methane (CH₄) derived from internal metabolism and external sources (Hotchkiss et al., 2015; Stanley et al., 2016). The rates at which streams emit carbon to the atmosphere reflects their importance in local and global carbon cycling. Streams emit CO₂ globally at a rate that surpasses the terrestrial and oceanic carbon sinks (Webb et al., 2018) and emit approximately 5% of yearly global CH₄ to the atmosphere (Flury & Ulseth, 2019; Stanley et al., 2016). As global concentrations of atmospheric greenhouse gases continue to rise, quantifying the relative contributions of different sources and sinks of CO₂ and CH₄ grows ever more important.

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The characteristics and gradients of a valley, particularly those in mountainous regions, create heterogeneous stream corridors that regulate the movement of water and carbon. Heterogeneous channel geomorphology and resulting patches within stream corridors offer diverse conditions for microbial metabolic processes. Some patches within stream corridors may disproportionately alter ecosystem carbon budgets, serving as “control points” for biogeochemical activity (Bernhardt et al., 2017; McClain et al., 2003). The path of stream water through pools, riffles, and subsurface connections determines how terrestrial carbon and soil-derived greenhouse gases are received and processed (Bowden & Bormann, 1986). Slower flowing pools allow organic matter to accumulate and be metabolized and oxygen to be depleted, making them conducive to CH₄ as well as CO₂ production (Sanders et al., 2007). Steeper or pinched reaches with faster flow emit greenhouse gases at a higher rate (Beaulieu et al., 2011). Surface flow continuity and hyporheic exchange may be disrupted because of slope failures, changing soil and bedrock properties, large root systems, lack of precipitation, and other geomorphic features (Boano et al., 2013). Ever-changing connections between patches in corridors, and the subsequent delivery of carbon (Corson-Rikert et al., 2016) and nutrients (Butturini & Sabater, 2000) to streams, affect the spatial and temporal heterogeneity of stream greenhouse gas emissions (Cole & Caraco, 2001). Precipitation and changing flow paths fill and drain ephemeral pools that can be present near streams, even in mountainous regions. Changes in flow create transient connections among features of the watershed that provide sources or loss pathways for dissolved greenhouse gases. Recent advances in river corridor science have pointed to the importance of hyporheic exchange and subsurface biogeochemistry (Harvey & Gooseff, 2015; Stegen et al., 2018) in combination with hydrologic forcing (Schmadel et al., 2017; Ward et al., 2019) to explain variations in ecological function along flowing waters. The biogeochemical signatures of an entire stream corridor are thus a function of how stream, vernal pool, and terrestrial components are formed and connected by variable flows.

One central challenge in estimating stream corridor greenhouse gas emissions is identifying the patterns of carbon emissions within and among corridor patches. To start, there is limited availability of high resolution spatial and temporal $p\text{CO}_2$ and $p\text{CH}_4$ data from geographically and geomorphically diverse stream reaches and nearby freshwater patches. Constraints from low spatial resolution sampling as well as uncertainty around estimates of air-water gas exchange rates often compound upon one another in attempts to upscale from sampling site to landscape carbon budgets (Webb et al., 2018). The consequences of the presence of vernal pools on carbon emissions from adjacent flowing waters have been particularly understudied, with much work on riparian soil CO₂ contributions to stream carbon fluxes coming from peatland-stream interfaces (Campeau et al., 2018; Hope et al., 2004; Leith et al., 2015). However, there remains a lack of data from temperate systems to test the influence of multiple freshwater patches on corridor exchange and the consequences for carbon emissions. Since first order streams account for more than 50% of all river networks by length (Downing et al., 2012), inaccurately characterizing their connections to adjacent patches and resulting greenhouse gas contributions to the atmosphere leaves a considerable gap in attempts to upscale emissions estimates.

In this study, we investigated greenhouse gas dynamics of heterogeneous stream corridors within a forested, mountain landscape. We (a) measured the heterogeneity of stream CO₂ and CH₄ concentrations and emissions within and between four stream corridors, (b) measured emissions from vernal pools, riparian hillslope, and dry bed patches along streams where available, and (c) tested how integrating different ecosystem patches within a stream corridor affects upscaling CO₂ and CH₄ emissions. By exploring diverse stream corridor and channel patches within subcatchments, we aimed to capture a more representative story of stream carbon emissions and variability from southeastern hardwood forest streams.

2. Methods

2.1. Study Site

We characterized greenhouse gas dynamics across four subwatersheds during the summers of 2018 and 2019 at Coweeta Hydrologic Laboratory in the Blue Ridge Mountains of North Carolina in the United States (Figure 1). The region is temperate and humid; yearly precipitation averages 179 cm, peaking in the winter and early spring, and snow is infrequent (Laseter et al., 2012). Coweeta received 172 mm of rain during the 2018 summer study period compared to 108 mm during the summer of 2019. Max daily precipitation during summer 2018 was 33 mm and in summer 2019 was 22 mm. Mean summer and annual

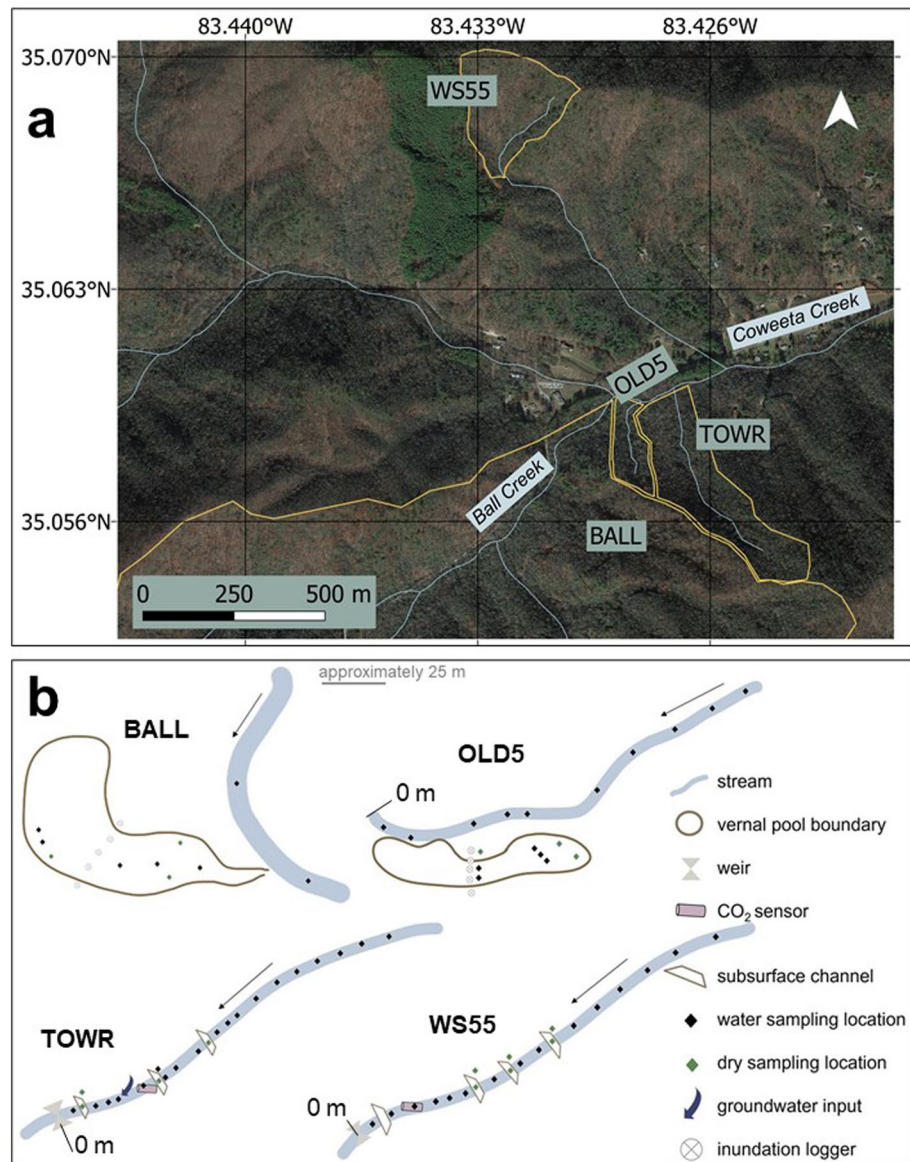


Figure 1. (a) Map showing study streams within their subwatersheds: BALL = Ball Creek, OLD5 = Old 5 watershed, TOWR = Watershed 5b, WS55 = Watershed 55. (b) Site sketches of each stream corridor showing sampling locations, sensors, and channel features.

air temperatures are 21.3°C and 12.9°C, respectively (Burt et al., 2018). Vegetation throughout the subwatersheds within the Coweeta basin is approximately 90 year old oak-hickory and northern hardwood forests (Laseter et al., 2012). Soils are shallow but tend to have high organic matter content (5%–14% (USDA NRCS, 2021)), and the steep, high elevation topography exposes metamorphic rock (granite gneiss and mica schist) (Jensen et al., 2017; Laseter et al., 2012).

Our research took place along four stream corridors with distinct ecosystem patches in the Coweeta basin (Table 1, Figure 1). We sampled Watershed 55 (WS55), which has the steepest upstream-downstream channel gradient (24 cm m⁻¹), close to its origin. Watershed 5b (TOWR) and Old 5 (OLD5) streams have shallower slopes, and OLD5 has an adjacent vernal pool near its confluence with Coweeta Creek. TOWR, WS55, and OLD5 are each first order streams with average depths less than 10 cm. Ball Creek (BALL) is a second order stream (10–30 cm deep) that crosses nearly the full length of the Coweeta watershed; near its confluence with Coweeta Creek, the BALL corridor also includes vernal pools. The TOWR stream is part

Table 1
Stream Corridor Characteristics

Stream corridor (abbreviation)	Patch types in the corridor	Summer studied	Elevation (m)	Catchment area (km ²)	Lat/Long (DD)
Watershed 55 stream (WS55)	Stream (1st order), dry streambed, hillslope	2018, 2019	819	0.08	35.06829, -83.43224
Watershed 5b stream (TOWR)	Stream (1st order), dry streambed, hillslope	2018, 2019	713	0.07	35.05780, -83.42696
Old 5 stream (OLD5)	Stream (1st order), vernal pool, dry pool	2018, 2019	702	0.19	35.05830, -83.4283
Ball Creek (BALL)	Stream (2nd order), vernal pool, dry pool, hillslope	2019	685	7.28	35.05866, -83.42968

Note. Elevation and coordinates are for top of the study reach.

of an ongoing whole-stream warming experiment where the temperature of the stream will be elevated by 3°C above ambient stream water for at least two years. The warming apparatus was not installed in 2018 and ramp-up to the experimental warming started in June 2019. We found no evidence to suggest that early experimental warming altered TOWR greenhouse gas emissions at the corridor scale.

We sampled multiple patches within each stream corridor. A “stream” designation describes flowing surface water. Dry streambed patches refer to locations within the defined stream channel where no surface water was present. In the three first order streams (WS55, TOWR, OLD5) dry streambeds occurred where water preferentially flowed in subsurface channels at the time of sampling. Along approximately 150–200 m study reaches of OLD5, TOWR, and WS55, we selected stream and dry bed sampling sites that captured the diversity of each corridor’s channel morphology. Hillslope patches were forest soils adjacent to the stream but within high water marks. Vernal pool patches were areas of ponded water standing over organic-rich soils; two pools were adjacent to the OLD5 and BALL streams (one by each stream). At the beginning of summer 2019, both vernal pools had surface connections to streams; however the BALL stream-pool surface connection dried by July, and the OLD5 stream-pool surface connection was gone in August (Figure 1b). Throughout this paper, we will use “stream” to refer only to our stream patches of flowing surface water, while “corridor” will refer to the collection of patches (stream, dry bed, hillslope, and pool). Not all patch types were present in each corridor (Table 1). For upscaling calculations described below, the corridor includes the stream surface water and dry beds, 1 m of hillslope on either side of the water’s edge, and vernal pool wetted area at the maximum observed extent in June.

In summer 2018, we sampled TOWR and WS55 streams and dry streambed sites in June and August. OLD5 stream sites were also sampled only in August of 2018, but during all 3 months of 2019 though at fewer sites. During 2019, all corridors (and patches within them, where present) were sampled once per month in June, July, and August. Vernal pool patches were only sampled in 2019. We also sampled upstream and downstream of a known groundwater input into the TOWR stream. At OLD5 and BALL, we sampled sites upstream and downstream of ephemeral vernal pools (Figure 1b). Within each of the vernal pools we sampled locations across a transect of different water depths (2–10 cm); in August when standing water in the vernal pools completely receded, we sampled fluxes over smooth sediments across and near the edges of the depressions where airtight chamber seals were possible.

We assembled environmental data from streams and around the catchment. At every discrete sampling event, we measured surface water temperature (YSI ProSolo Optical Dissolved Oxygen and Conductivity Meter) and pH (Orion Portable pH Meter) in each stream and vernal pool. We took elevation readings at each sampling site using a GPS unit (Garmin GPSMap 64 Handheld Outdoor). Precipitation data were obtained from Coweeta recording rain gauge 06 (described in Miniati et al., 2017). We measured vernal pool inundation using modified temperature/light loggers (ONSET HOBO Pendant) to detect presence or absence of surface water (Chapin et al., 2014).

2.2. Dissolved Gas Concentrations

We sampled stream and vernal pool water for dissolved gases using a syringe headspace equilibration method (Halbedel, 2015), taking triplicate samples at each site. We drew 80 mL of bubble-free surface water and 40 mL of ambient air into a 120 mL syringe (JMS JS-S00L) fitted with a 3-way stopcock (DWK Life Sciences Kimble Kontes FlexColumn). We shook each sample for 3 min. We injected headspace samples into sealed 20 mL vials (DWK Life Sciences MicroLiter 20 mm) filled with ambient air using simultaneous injection and flushing to displace ambient air with our sample volume. Our tests of this sampling method recovered 93% of CH₄ and 101% of CO₂, compared with an analytical error of ±3.1 and ± 2.2%, respectively. We analyzed headspace samples and ambient air samples for CO₂ and CH₄ on a gas chromatograph (Shimadzu Nexis GC-2030) fitted with both a thermal conductivity and flame ionization detector.

We estimated the partial pressure of CO₂ and CH₄ in stream and vernal pool water from GC analyses as (Equation 1):

$$C_{\text{gas}_i \text{ water}} = \text{BP} \cdot \frac{\text{vol}_{\text{air}} \left(\text{ppmv}_{\text{gas}_i \text{ eq}} - \text{ppmv}_{\text{gas}_i \text{ air}} \right)}{\left(R \cdot T \cdot \text{vol}_{\text{H}_2\text{O}} \right) + H^\ominus \cdot e^{\left(\frac{-\Delta_{\text{sol}} \cdot H}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right)}} \cdot \text{ppmv}_{\text{gas}_i \text{ eq}} \quad (1)$$

The concentration of CO₂ or CH₄ dissolved in the water ($C_{\text{gas}_i \text{ water}}$, mol m⁻³; where gas_i is either CO₂ or CH₄ throughout) is a function of barometric pressure (BP, kPa), volume of air added for headspace equilibration (vol_{air} , m⁻³), measured concentration of gas_i in the equilibrated headspace (after mixing air and water, accounting for the volume and temperature of the sample water using Henry's law constant for gas_i at water temperature and partial pressure of the gas_i in the air) ($\text{ppmv}_{\text{gas}_i \text{ eq}}$ ppm), the measured concentration of gas_i in the air used as headspace ($\text{ppmv}_{\text{gas}_i \text{ air}}$ ppm), the universal gas constant (R , m³ kPa K⁻¹ mol⁻¹ [converted from L atm K⁻¹ mol⁻¹]), headspace temperature (T , K), the volume of water equilibrated ($\text{vol}_{\text{H}_2\text{O}}$ m³, and Henry's law constant H^\ominus at a standard temperature (298.15 K) for gas_i converted to headspace temperature $\left(-\Delta_{\text{sol}} \cdot H/R \right)$ (Henry's law constants for CO₂ and CH₄ from Sander, 2015; method adapted from Demarty et al., 2011).

During the summer of 2019, we deployed one underwater CO₂ sensor (eosGP, Eosense) at fixed points (35 m upstream from the weirs) in each of the TOWR and WS55 streams. We programmed the sensor to log every 30 min using Campbell dataloggers (CR1000) powered by marine batteries (Optima, Model 034). We used in-stream dissolved CO₂ concentrations from discrete samples and headspace equilibration (Equation 1) to calibration-correct the sensor measurements assuming linear drift during the sensor deployment period.

2.3. Emission Fluxes

We measured the emission flux of CO₂ and CH₄ to the atmosphere from the surface of first order streams and their riparian hillslopes and vernal pools. We connected a portable infrared gas analyzer (Los Gatos Research Ultra-Portable Gas Analyzer) to a small chamber (volume = 214 cm³, surface area = 38.4 cm²) with airtight tubing. We placed the floating chamber directly on the surface of the water in stream and vernal pool patches to form a seal atop the water, gently holding it place (Campeau et al., 2014). The small channel width, steep gradients, shallow depth, and the presence of rocks and detritus prevented use of a fully floating chamber technique, but turbulence was low enough to allow for semi-anchored chambers to create an air-tight seal at the water surface. To sample dry bed, dry vernal pool soil, and hillslope patches, we selected sites where chamber placements on the ground were airtight. We monitored flux in real time (5-s intervals) as the chamber was held in place long enough to see a linear change in CO₂ and CH₄ concentration but before concentrations leveled out (up to 5 min). We calculated fluxes (Equation 2) by estimating the slope from a linear regression of chamber concentrations of CO₂ and CH₄ over time, and then we converted each chamber measurement to an areal flux (C flux gas_i, mol m⁻² d⁻¹):

$$\text{C flux gas}_i = \left(\frac{\text{Flux}_{\text{chamber}}}{R \cdot T \cdot \frac{1}{\text{BP}}} \right) \cdot \frac{V}{SA} \quad (2)$$

where $\text{Flux}_{\text{chamber}}$ (ppm d^{-1}) is the change in gas concentration over time, and chamber volume (V) and surface area (SA) units are m^3 and m^2 , respectively. R , T , and BP are the same as Equation 1.

At several surface water sampling points in each corridor, we took both dissolved gas flux and concentration measurements at the same location. By rearranging Equation 3, we calculated the average and range of gas transfer velocity values for a given stream reach or vernal pool sampling location:

$$\text{Emissions}_{(i,s)} = \left[C \text{ gas}_i \right]_{\text{water}} \cdot k_s \quad (3)$$

where i is CO_2 and k_s (m d^{-1}) is the site-specific gas transfer velocity. We used only paired CO_2 flux and concentration measurements because of the flat slope of CH_4 fluxes we found at many stream sites. We paired flux and concentration measurements at 26 sampling locations. Once we characterized k , we standardized k values to a constant temperature to get gas transfer velocity with a Schmidt number of 600 (k_{600}) after Raymond et al. (2012) using Equation 4:

$$k_{600} = \left(\frac{600}{Sc_{\text{CO}_2}} \right)^{-0.5} \times k_{\text{CO}_2} \quad (4)$$

We applied median site-specific k_{600} estimates to measurements of dissolved gas concentrations to convert CO_2 and CH_4 concentration $[C\text{gas}_i]$ or $[\text{CO}_2 \text{ or } \text{CH}_4]_{\text{water}}$ (mol m^{-3}) to emission fluxes ($\text{mol m}^{-2} \text{d}^{-1}$). For Ball Creek stream flux estimates, we estimated k_{600} based on stream channel characteristics, as in Raymond et al. (2012).

2.4. Analyses

To assess the relative importance of the presence of a vernal pool and other stream corridor patches to first order stream corridor emissions, we calculated patch area-weighted fluxes (Equation 5) for the first order corridors: OLD5, TOWR, and WS55.

$$C \text{ flux gas}_i \text{ corridor} = \sum_{\text{for 1 to } x \text{ patch types}} C \text{ flux gas}_i \text{ patch } x \cdot \left(\frac{\text{area}_{\text{patch } x}}{\text{area}_{\text{corridor}}} \right) \quad (5)$$

$C \text{ flux gas}_i \text{ [patch } x]$ (where i is either CO_2 or CH_4 and x is patch type) is the median flux value ($\text{mmol m}^{-2} \text{d}^{-1}$) from a specific patch in one corridor from all sampling events (e.g., the OLD5 vernal pool); $\text{area}_{\text{[patch } x]}/\text{area}_{\text{[corridor]}}$ (m^2/m^2) is the area occupied by the specific patch divided by the total area of the corridor, which gives percent area with which to weight median corridor-specific estimates. The corridor includes the stream surface water and dry beds, 1 m of hillslope on either side of the water's edge, and vernal pool wetted area at the maximum observed extent in June. We did not include the BALL stream corridor in this analysis because we lacked the spatial resolution for BALL samples and because it is a much larger stream. Focusing on first order corridors additionally allowed us to calculate patch area-weighted fluxes for an average first-order stream corridor in the Coweeta basin that included relevant proportions of all 5 patch types, thus representing their average prevalence among all sites. We totaled the total areas and patch-specific areas of the 3 first order corridors. Using the median emissions values from the different first order patches, we calculated a proportional emissions contribution from each first order patch type, and we summed those patch contributions to estimate carbon flux for this average corridor.

We used one-way analyses of variance (ANOVA) to test for differences in the magnitude and variance of fluxes among sampling corridors, time periods (year, month), and patch types. We then used Tukey Honest Significant Differences to compare the means within groups with significant differences (corridors, year, and patch types). We conducted all statistical analyses using R (version 1.1.463; R Core Team, 2018).

3. Results

3.1. k_{600} Estimations

We found k_{600} values varied more from first order streams than they did from vernal pools (Table S3). WS55 had higher gas transfer velocities (median 5.93, range 2.41–13.6 m d^{-1}) than the TOWR stream (median

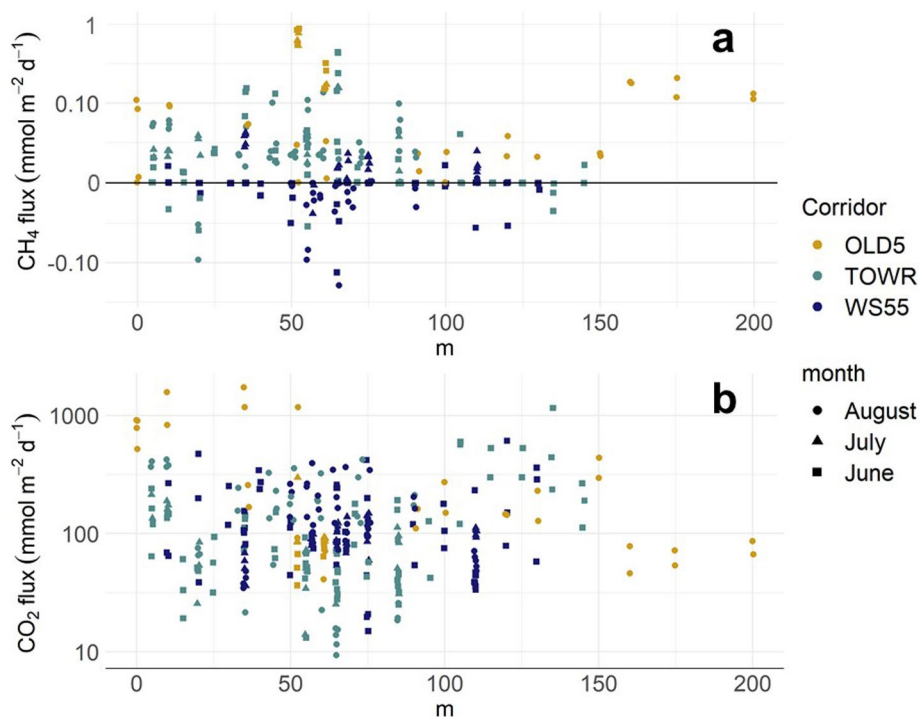


Figure 2. Spatial emission fluxes of CH₄ (a) and CO₂ (b) from first order streams in Coweeta, NC, USA. Emission estimates are organized from downstream (0 m) to upstream (150 m) on the x axis. Sampling months (in 2018 and 2019) are noted with different shapes: squares (June), triangles (July), and circles (August). Shading color corresponds with stream corridor (OLD5, TOWR, WS55). Meter marks denote either distance upstream from a weir (WS55, TOWR) or the farthest downstream point before a confluence with a larger stream (OLD 5) and are intended only as visual aids for longitudinal distance and variability, not to relate distances from different streams to each other. Please note log-transformed y-axes.

3.56, range 0.667–9.02 m d⁻¹; $F_{1,22} = 3.59$, $p = 0.04$) as was expected due to its steeper slope. Vernal pool k_{600} values (median 1.49, range 1.29–4.6 m d⁻¹) were not significantly lower than k_{600} estimated for stream sites; ($F_{1,26} = 3.75$, $p = 0.30$).

3.2. Spatial and Temporal Heterogeneity of Greenhouse Gas Emissions in Streams

CH₄ fluxes varied over space both within streams (Table S4, $p < 0.05$ for each of the 1st order streams) and among corridors ($F_{3,298} = 34.8$, $p < 0.001$): some sampling sites were reliably CH₄ sources, while others were consistently CH₄ sinks (Figure 2). There was no clear correlation of greenhouse gas flux with temperature from any stream ($F_{1,302} = 0.15$ for CH₄ and $F_{1,330} = 0.55$ for CO₂). The WS55 stream was a sink of CH₄ for half of 147 measurements, and the median flux was -0.001 mmol m⁻² d⁻¹, but on 73 occasions it was a small source of CH₄ to the atmosphere (full range for CH₄ in WS55 stream -0.193 – 0.043 mmol m⁻² d⁻¹). The TOWR stream was usually a source of CH₄, but individual sampling sites were less likely to be consistent sources or sinks (median = 0.021; range -0.092 – 0.443 mmol m⁻² d⁻¹). The OLD5 stream was a much greater source of CH₄ than the other first order streams, with emissions ranging from 0.006–4.57 mmol m⁻² d⁻¹ (median = 0.11 mmol m⁻² d⁻¹; $p_{\text{adj}} < 0.001$ compared to TOWR and $p_{\text{adj}} < 0.001$ compared to WS55). While some individual sampling sites were distinctly different from one another within each of the first order streams, there was no longitudinal pattern of CH₄ emission magnitude along any of the 3 first order stream reaches. The second order stream, BALL was a source of CH₄ (median = 0.059; range 0.020–0.165 mmol m⁻² d⁻¹), though significantly less so than the OLD5 stream ($p_{\text{adj}} = 0.01$).

Streams were always sources of CO₂ and the magnitude of CO₂ emissions was heterogeneous over the length of each stream (Figure 2b; Table S4, $p < 0.001$ for sampling sites within each streams). Stream CO₂ emissions

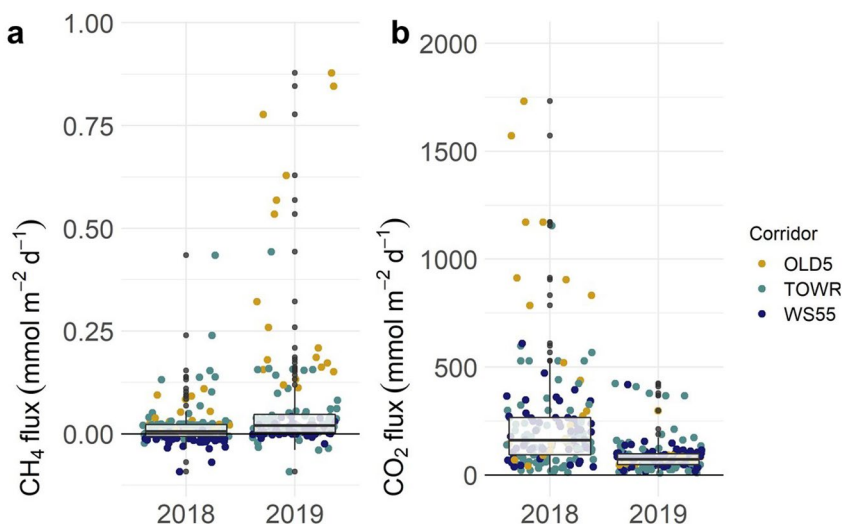


Figure 3. Coweeta stream CH₄ (a) and CO₂ (b) fluxes by year from first order study streams at Coweeta. Shading color corresponds with stream corridor (OLD5, TOWR, WS55).

also differed among the 4 corridors ($F_{3,328} = 12.3$, $p < 0.001$). The OLD5 stream was distinct from TOWR and WS55 in that there was a longitudinal pattern with higher CO₂ fluxes near its outlet ($F_{1,27} = 7.90$, $p < 0.001$ for sampling sites near the outlet compared to upstream). The OLD5 stream also had higher CO₂ emissions than TOWR and WS55 streams ($p_{\text{adj}} = 0.000001$ and 0.000000 , respectively; Table S4). There was no difference between TOWR and WS55 CO₂ emissions ($p_{\text{adj}} = 0.94$) nor was there any spatial pattern in emissions from either of the two streams. Median CO₂ emissions from OLD5, TOWR, and WS55 streams were similar: 110, 78, and 99 mmol m⁻² d⁻¹, respectively. The ranges of emissions from OLD5 (36–1,733 mmol m⁻² d⁻¹) and TOWR (9–1,155 mmol m⁻² d⁻¹) streams were much greater than WS55 (15–610 mmol m⁻² d⁻¹). While median CO₂ emissions estimates from BALL were similar to but less variable than the first order streams at 131 mmol m⁻² d⁻¹ (range 9–192 mmol m⁻² d⁻¹), overall CO₂ emissions from BALL were lower than OLD5 ($p_{\text{adj}} = 0.0006$) but not different than TOWR ($p_{\text{adj}} = 0.94$) or WS55 ($p_{\text{adj}} = 0.99$).

Stream CO₂ and CH₄ concentrations and emissions were less variable over time than they were among different sampling locations within streams. Emissions of CO₂ and CH₄ from streams remained relatively stable despite decreases in flow during summer 2019. There were no differences in CO₂ ($F_{2,259} = 0.4$, $p > 0.05$) or CH₄ ($F_{2,228} = 2.8$, $p > 0.05$) emissions when comparing monthly estimates from surface water in 2019 (Figure 3). Interestingly, stream CO₂ emissions were lower in 2019 than in 2018 ($F_{1,331} = 14.6$, $p < 0.001$; median emissions 76 and 160 mmol m⁻² d⁻¹, respectively), while CH₄ fluxes were not significantly different in 2018 versus 2019 ($F_{1,296} = 2.11$, $p > 0.05$; Figure 3b).

The lack of temporal trend in CO₂ emissions estimates over the summer was supported by high-frequency CO₂ sensor data from the TOWR and WS55 streams (Figure 4). In WS55, the variation in sensor dissolved CO₂ over time was comparable to the variation among discrete sampling locations within the 100 m reaches over the same time period (WS55 sensor range: 337–1,383 μatm, WS55 discrete: 228–1,462 μatm). For the TOWR stream, however, sensor dissolved CO₂ at a single site was less variable than discrete sample concentrations throughout the study reach (TOWR sensor range: 435–587 μatm, TOWR discrete: 247–3,503 μatm).

3.3. Patch Influences on Stream Corridor Emissions

Patches played distinct roles in corridor CO₂ and CH₄ fluxes across the Coweeta basin (Figure 5; $F_{4,429} = 11.62$ for CO₂, $F_{4,397} = 5.227$ for CH₄, $p < 0.001$ for both; Table S5 and S6). Median CO₂ and CH₄ fluxes to the atmosphere were higher from inundated (246 and 1.95 mmol m⁻² d⁻¹, for CO₂ and CH₄ respectively) and dry (277 and 0.239 mmol m⁻² d⁻¹) vernal pool patches than from stream surface waters (97 and 0.015 mmol m⁻² d⁻¹) or dry streambeds (78 and -0.009 mmol m⁻² d⁻¹). The median CO₂ emissions from inundated vernal pools was more than double that of streams (247 and 97 mmol m⁻² d⁻¹, respectively; $p_{\text{adj}} = 0.003$),

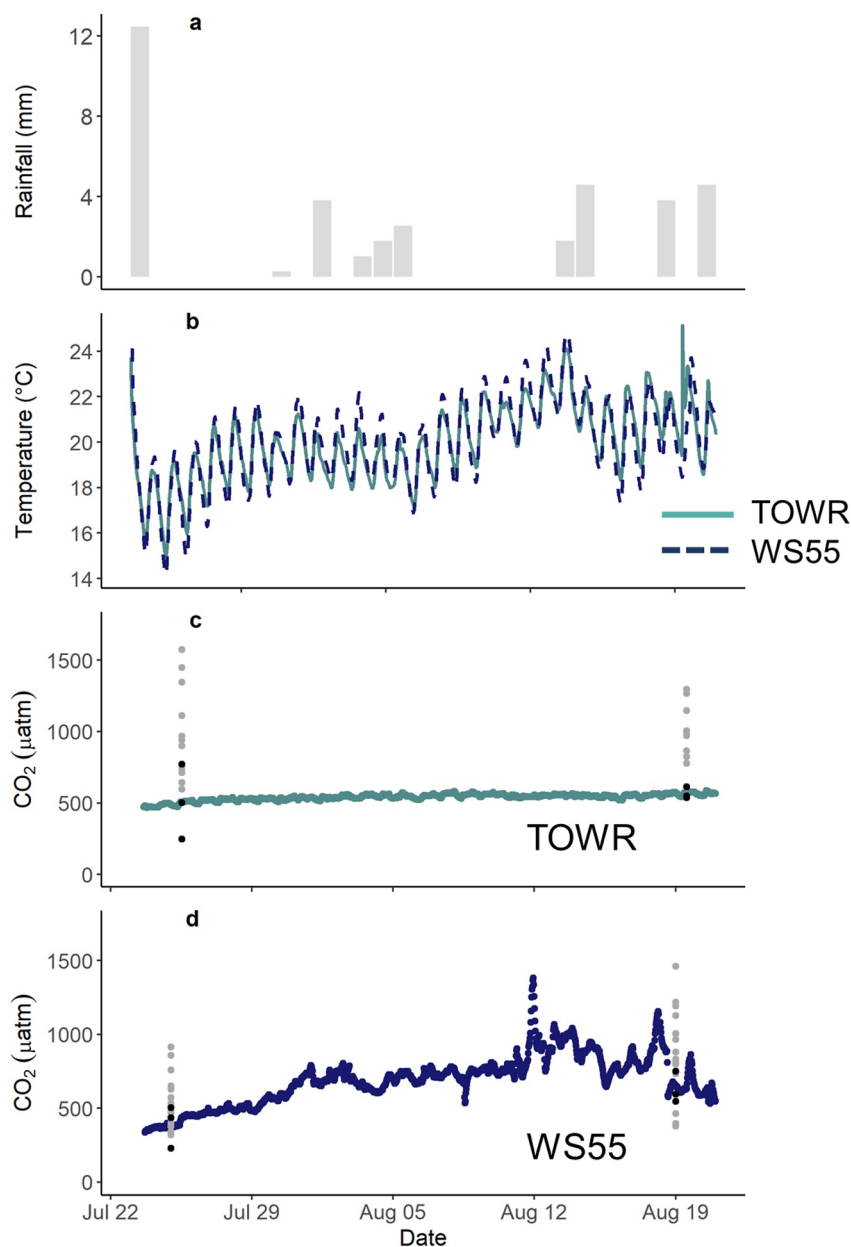


Figure 4. Local precipitation (a; daily, from Coweeta RG06 at the bottom of the basin), water temperature (b, green line TOWR, blue dashed WS55), and dissolved CO₂ concentrations over July and August of 2019 in TOWR (c) and WS55 (d) streams. Colored points are from sensor measurements at one location (35 m mark in each stream), while gray and black points show discrete CO₂ measurements from the locations along the entire sampled reach for July and August 2019; black points are discrete samples taken at the 35 m mark next to the sensor.

while median CH₄ emissions from vernal pools were over 2 orders of magnitude greater than that of streams (37 and 0.067 mmol m⁻² d⁻¹, respectively; $p_{\text{adj}} = 0.00008$). Only one measurement captured a negative flux (i.e., a CH₄ sink) at a sampling site nearer the edge of one vernal pool. The OLD5 vernal pool had higher CH₄ emissions than the BALL vernal pool ($p_{\text{adj}} = 0.005$), but the two pools had similar CO₂ emissions ($p_{\text{adj}} = 0.75$). CO₂ emissions from dried vernal pool surfaces were higher than those from inundated vernal pool areas ($p_{\text{adj}} = 0.008$), but CH₄ emissions from dry versus inundated vernal pools were not different ($p_{\text{adj}} = 0.58$). Dry stream bed CH₄ emissions were highest from the TOWR corridor ($p_{\text{adj}} = 0.05$); CO₂ emissions from TOWR and WS55 dry beds were more similar ($p_{\text{adj}} = 0.06$). Riparian hillslopes were typically sinks of CH₄ (median -0.050 mmol m⁻² d⁻¹, range -0.308 – 0.434) and sources of CO₂ (259 mmol m⁻² d⁻¹,

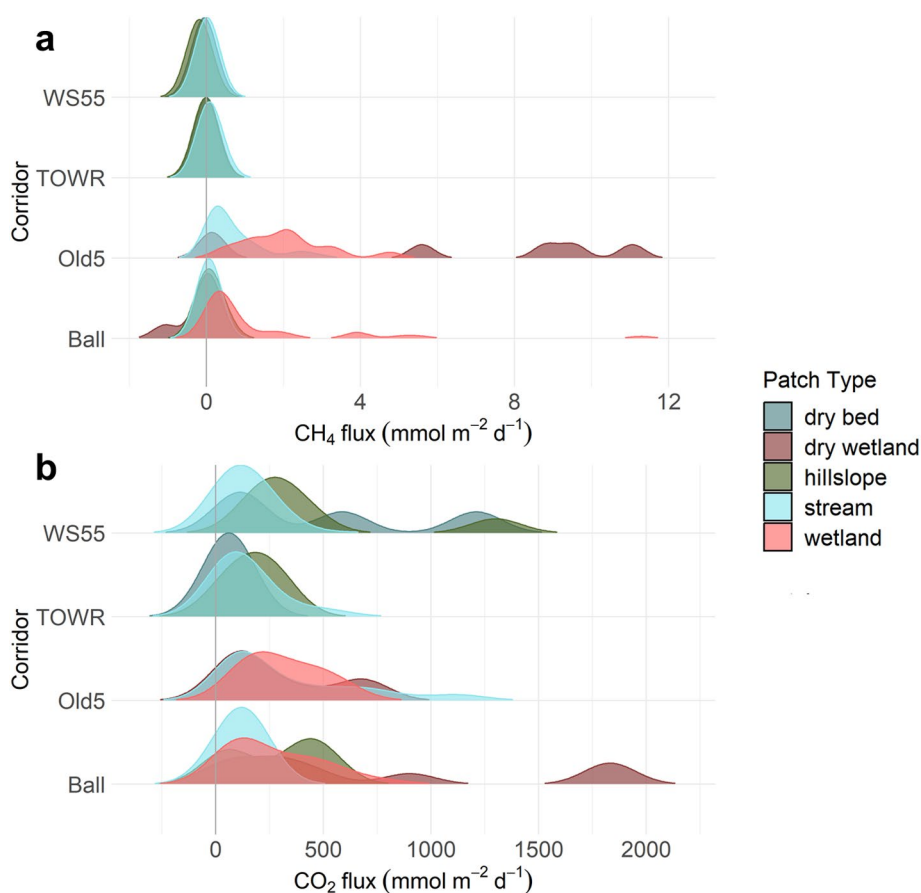


Figure 5. Distributions of patch CH₄ (a) and CO₂ (b) emissions from all 4 stream corridors. Note the different x axis scale. Please see Table S1 for number of measures from each corridor and patch type.

range 41–1,300), but did not differ significantly from streams ($p_{\text{adj}} = 0.09$ for CO₂ and $p_{\text{adj}} = 1.0$ for CH₄) or vernal pools ($p_{\text{adj}} = 0.99$ for CO₂ and $p_{\text{adj}} = 0.13$ for CH₄). Hillslope CH₄ emissions were higher from the TOWR corridor ($p_{\text{adj}} = 0.002$), but, as with dry beds, the TOWR and WS55 hillslopes had similar CO₂ emissions ($p_{\text{adj}} = 0.15$).

Different corridors had unique emissions signatures, and the presence of vernal pools had a significant influence over corridor greenhouse gas emissions. In addition to differences in emission magnitudes from different patch types, there was also a significant difference among the four corridors for both gases ($F_{3,430} = 13.46$ for CO₂, $F_{3,398} = 6.05$ for CH₄, $p < 0.001$ for both). The first order stream corridor with vernal pool patches present, OLD5, had higher CO₂ and CH₄ emissions than corridors without vernal pools ($F_{1,330} = 20.52$ for CO₂, $F_{1,302} = 32.16$ for CH₄, $p < 0.001$ for both; Table S7). Comparing emissions from different first order stream corridors (Tables 2–4) further illustrates the outsized impact of the vernal pools, especially on CH₄ emissions. Within the OLD5 corridor, we can isolate the effect of changing stream-vernal pool connections over summer 2019. Two stream sampling sites on OLD5, 52 and 61 m, were just downstream of where the vernal pool first entered the stream. These sites had higher emissions of CH₄ in June and July than in August of 2019 ($p_{\text{adj}} = 0.00008$ for June vs. August and $p_{\text{adj}} = 0.001$ for July vs. August). By August 2019, the OLD5 vernal pool had almost completely dried (Figure S2), so the surface aquatic connection from stream to vernal pool at those sampling sites was lost. Consequently, August CH₄ emissions from stream sites were more similar to emissions from upstream of the vernal pool sampling sites on OLD5 in 2019 and from the TOWR and WS55 streams.

Table 2

Patch Areas (m²) for Coweeta First Order Stream Corridors: Wetted Stream Study Reach, Dry Stream Bed (Measured August 2018), Vernal Pool (Measured June 2019), Dry Pool (Measured August 2019), Hillslope on 1 m of Either Side of Stream Channel, and Total Corridor Area

	Stream	Dry bed	Vernal pool	Dry pool	Hillslope	Total corridor
OLD5	200	-	262	58	-	520
TOWR	174	26	-	-	400	600
WS55	189	11	-	-	400	600
All 1st order stream corridors	564	36	262	58	800	1,720

Note. Dashes indicate no data because that patch type was not present in the corridor.

4. Discussion

We investigated the magnitude and variability of CO₂ and CH₄ emissions within and among stream corridors. Corridor greenhouse gas emissions were variable over space, particularly when comparing emissions from different patches. Emissions of CO₂ and CH₄ from stream surface waters in particular were heterogeneous along our study reaches, even over distances of less than 10 m. We conducted this research over two summers in 2018 and 2019, the latter of which was unusually dry for the humid southeastern Appalachians. The dryness of 2019 provided an interesting opportunity to measure stream corridor CO₂ and CH₄ flux under diminished water levels. Stream water CO₂ emissions from all corridors were lower in 2019 but did not vary much within either summer. There was no effect of temperature on greenhouse gas fluxes within summer months. Finally, the first order stream with an adjacent vernal pool in its corridor had elevated carbon emissions compared to the first order streams without vernal pools, with highest emissions downstream of adjacent vernal pools. Streams and riparian vernal pools both contributed substantially to corridor carbon emissions, while hillslope and dry bed sites were sources of CO₂ but not always CH₄. Our integrated corridor emissions estimates reflect the diversity of ecosystem patches surrounding fresh waters.

All streams were sources of CO₂ to the atmosphere, and all but one were CH₄ sources. Stream CO₂ emissions were comparable to values reported for other forested first order streams in the southeastern United States (146 mmol m⁻² d⁻¹ in Jones & Mulholland, 1998a compared to our median of 94.3 mmol m⁻² d⁻¹). Our median CH₄ estimate was 0.013 mmol m⁻² d⁻¹, which was at the lower end of the range for CH₄ emissions from forested streams (range 0.001–100 mmol m⁻² d⁻¹ in Stanley et al., 2016). The WS55 corridor was unusual in its undersaturation of CH₄ compared to the atmosphere. While not unprecedented for fluvial ecosystems (Stanley et al., 2016), CH₄ sinks on the landscape are more commonly associated with forest soils. The valley and channel gradient of the WS55 subcatchment may be responsible for stream CH₄ undersaturation: with lower organic matter and fewer sources of CH₄, water flowing over steep gradients remains well oxygenated allowing CH₄ oxidation to use what little CH₄ is available. In reaches of small streams with high spatial variability in CH₄ production and oxidation, sediment nitrogen content was positively correlated with CH₄ production and oxidation (Bodmer et al., 2020). Because stream nitrogen concentrations vary among sub-watersheds at Coweeta and over time, with forested streams typically having low stream nitrogen (Knoepp

Table 3

Median Stream Corridor CH₄ Emissions (mmol m⁻² d⁻¹; Range in Parentheses) From Patch Types in First Order Stream Corridors, Including Dry Stream Bed, Vernal Pool, Dry Pool, Hillslope, and for the Full Corridor Median Weighted by Patch Areas

	Stream	Dry bed	Vernal pool	Dry pool	Hillslope	Weighted corridor by area
OLD5	0.095 (0.006–4.57)	-	2.53 (0.371–733)	9.18 (0.044–36.7)	-	2.32
TOWR	0.021 (–0.092–0.443)	0.003 (–0.039–0.007)	-	-	–0.021 (–0.059–0.015)	–0.008
WS55	–0.001 (–0.193–0.043)	–0.042 (–0.152–0.019)	-	-	–0.161 (–0.308–0.086)	–0.108
All 1st order stream corridors	0.013 (–0.193–4.57)	–0.009 (–0.152–0.007)	2.53 (0.371–733)	9.18 (0.044–36.7)	–0.05 (–0.308–0.015)	0.679

Note. Data are from all measurements over both study summers.

Table 4

Median Stream Corridor CO₂ Emissions (mmol m⁻² d⁻¹; Range in Parentheses) From Patch Types in First Order Stream Corridors, Dry Stream Bed, Riparian Ephemeral Vernal Pool, Dry Pool, Hillslope, and for the Full Corridor Median Weighted by Patch Areas

	Stream	Dry bed	Vernal pool	Dry pool	Hillslope	Weighted corridor by area
OLD5	111 (36.5–1,730)	-	247 (114–557)	163 (33.2–701)	-	178
TOWR	79.4 (9.38–1,160)	55.2 (44.1–81.9)	-	-	187 (41.1–288)	150
WS55	99 (15–610)	366 (80.9–1,210)	-	-	301 (164–1,300)	240
All 1st order stream corridors	94.3 (9.38–1,730)	78 (44.1–1,210)	247 (114–557)	163 (33.2–701)	259 (41.1–1,300)	186

Note. Data are from all measurements over both study summers.

& Swank, 1997; Webster et al., 2016), future work characterizing differences in sediment nutrient contents may provide valuable insights into drivers of CH₄ from our study streams.

CO₂ and CH₄ emissions were heterogeneous within stream reaches. We were unable to identify consistent trends in longitudinal spatial variability of CO₂ and CH₄ flux among small streams all nestled within the Coweeta basin. Spatial differences in emissions have been previously attributed to geomorphic controls, especially when channel geomorphology creates surface water and groundwater connections (Crawford, Loken, et al., 2017; Lupon et al., 2019; Smits et al., 2017). While our first order reaches had high variability in CO₂ and CH₄ emissions, we did not find consistent patterns of certain sampling points as sources or sinks of a particular magnitude. For example, in the TOWR stream, one sampling location at 65 m featured a bowl-like area of slower-moving water and sediment buildup. This location usually had higher CH₄ emissions than anywhere else along the stream; sometimes they were comparable to the high-emitting OLD5 stream sites nearest the vernal pool. However, emissions were not always significantly higher than other individual TOWR sampling sites, nor were they significantly higher than all other sampling locations in that stream put together. We do not believe in-stream primary production controlled local CO₂ heterogeneity because light and primary productivity are consistently low along first order forested streams in this region (e.g., Benstead et al., 2009; Greenwood & Rosemond, 2011). The lack of emission pattern based on geomorphic features may result from mechanisms that are at odds with one another acting on carbon emissions at an individual sites: slope (Jones & Mulholland, 1998b; Smits et al., 2017), weathering (Johnson et al., 2007; Jones & Mulholland, 1998a), and terrestrial inputs (Dinsmore et al., 2013) all contribute to the biogeochemical and physical processes acting on carbon fluxes. It is notable that CO₂ emissions from the second order stream, Ball Creek, were less variable than those from the first order streams, indicating that the signals of mechanisms creating higher spatial heterogeneity in first order streams may become diluted in higher order streams. Future work that includes more spatially expansive paired flux and concentration data will help link physical and chemical corridor characteristics when upscaling carbon emissions beyond the reach scale.

Stream CO₂ emissions did not vary within summer months but differed between the two sampling years. We did not observe short term summer changes in emissions in response to lower precipitation periods, which contrasts with some previous work from streams (Crawford, Loken, et al., 2017; Wallin et al., 2020) and adjacent habitats (Hope et al., 2004; Jacinthe et al., 2015) where emissions tracked precipitation more closely. We expected that the lack of precipitation would deprive the stream of more soil-derived carbon (Dinsmore et al., 2013; Johnson et al., 2008). Groundwater connections among riparian soils and stream channels can support stable greenhouse gas emissions over time (Lupon et al., 2019). Organic matter and dissolved gas inputs from terrestrial sources and subsurface flow paths at our sites appear to have been sufficiently stable to minimize variability in patch-scale biogeochemical activity and emissions within a certain range during the summer months. Given that our sampling times were during peak terrestrial productivity, when high rates of evapotranspiration may reduce hydrologic connections between soils and streams, less soil-derived CO₂ may enter stream water, and stream flow and pCO₂ levels are likely maintained by groundwater from deeper subsurface flow paths (Jones & Mulholland, 1998b). Our finding of lower CO₂ emissions in the dryer summer of 2019 compared to summer 2018 are in agreement with work that has connected annual precipitation and fluvial CO₂ emission (Butman & Raymond, 2011; Öquist et al., 2014; Winterdahl et al., 2016). Lower CO₂ emissions during longer-lasting dry spells may have resulted from the lower rates of outgassing

we observed in 2019, which can control emissions in steep mountain streams (Marx et al., 2017). While wet-dry cycles can control carbon flux (Looman et al., 2017; McClain et al., 2003), our results provide additional evidence that year-to-year differences in precipitation may be more important drivers in some small streams than changes within a season.

Interestingly, the combination of in-stream logging CO₂ sensors and monthly CO₂ grab samples highlights three pivotal considerations when quantifying patterns of CO₂ emissions from headwater streams. First, isolated sampling events may bias stream CO₂ emissions because the timing of grab samples relative to storms or short term drying will sway resulting analyses (as noted by Crawford, Stanley, et al., 2017). We found that nearby first order streams can have contrasting patterns of spatiotemporal variability: WS55 grab samples along the length of the study reach had a smaller range in CO₂ concentrations than the sensor captured at a single location, but the TOWR sensor concentrations were remarkably constrained over time relative to the spatial variability along that stream. This brings us to the next consideration, which is that the contrasting CO₂ emissions patterns for headwater streams may not be limited to streams from different climatic zones or geographic provinces since we can see divergent patterns from streams less than 2 km apart. Finally, any single sampling location along a geomorphically heterogeneous stream reach may be a poor representative of the full stream's contributions to carbon flux.

The presence of vernal pools in a stream corridor had an outsized impact on corridor-scale carbon emissions. Vernal pool CO₂ and CH₄ emissions were high, but not different from the range of values reported for other freshwater wetlands and vernal pools (e.g., Bolpagni et al., 2017; Boon et al., 1997; Kifner et al., 2018). Riparian zones accumulate organic matter along streams, directly influencing the size (Ledesma et al., 2015) and arrangement (Leith et al., 2015; Teodoru et al., 2009) of connections between corridor patches and the stream channel, and thus shape corridor carbon fluxes. OLD5 was the only first order stream in our study that had an impermanent surface water connection to a vernal pool, but ephemeral pools are not uncommon in mountain or humid landscapes (Blackman, 2019; Lathrop et al., 2005; Wu et al., 2014). While there is little flat land for vernal pools to form upon in this region, not much riparian area is needed to effectively slow down water and retain soil moisture and organic matter in a way that steeply carved streams cannot. Our vernal pools share many characteristics with pools from other temperate regions, which are demonstrated hotspots of organic matter processing (Capps et al., 2014).

As vernal pools dried, we were able to observe higher CO₂ emissions from both vernal pools but different patterns in CH₄ emissions from OLD 5 and BALL. Surprisingly, some of our highest CH₄ emissions estimates came from dry vernal pool patches in OLD5, while BALL dry vernal pool patches more predictably emitted less CH₄. While there was a diminished area of standing water in the vernal pools during our August sampling trip in 2019, we did happen to sample after small rain showers (<5 mm). It is also of note that we never observed the sediments of vernal pool patches to be completely desiccated, likely due to the brief rain showers, humid climate, and heavy canopy shading of the patches. The OLD5 vernal pool area was particularly well covered by rhododendron compared to BALL. While aeration from drying should reduce methanogenesis due to changes in dissolved oxygen and redox state, it is possible to see brief surges of CH₄, before eventual longer term decreases in emissions, as water tables drop (e.g., as reported by Sturtevant et al., 2016 for a freshwater, restored vernal pool). Small vernal pools are sensitive to changes in hydrology (Blackman, 2019), and climate change is likely to increase incidence of extreme weather phenomena that could influence the formation and longevity of ephemeral waterbodies. The climate of the southeastern United States is predicted to shift closer to a Mediterranean climate (Karl et al., 2009), with mild, wet winters and dry summers that promote vernal pool formation (Keeley & Zedler, 1998). Given the impact of vernal pool patches on both stream reach and stream corridor carbon emissions, along with climatic changes that will create conditions conducive to their formation, mountain riparian vernal pools could become a more important component of freshwater ecosystem carbon emissions in the future.

Cycles of drying and rewetting control the flow and transformation of carbon within, through, and among patches along a stream corridor. The movement of water between patches transports resources across patch boundaries; ecosystem functions change as cross-patch connections are lost or fundamentally altered (Crawford et al., 2014; Schiff et al., 1990). The timing, quantities, and qualities of resource exchanges between patches have important consequences for biogeochemical cycling and greenhouse gas emissions (Abril & Borges, 2019; Tockner et al., 2000). Our study found that stream-vernal pool linkages can be significant

contributors to stream corridor carbon emissions. Our results also point to a future avenue of research in that the area of a vernal pool relative to an adjacent stream may predict how much the pool contributes to stream carbon emissions when connected—of our two similarly sized vernal pools, we only found that the vernal pool contributed emissions to the first order stream. However, many unknowns linger surrounding patterns of patch connectivity and comparisons among catchments. How distinct pathways and timings of resource movement among patches change with flow is an increasingly large knowledge gap given new precipitation patterns that are being observed due to climate change.

This project provides unique insights into the spatial and temporal complexities of estimating freshwater greenhouse gas emissions from stream corridors. Our results also highlight ongoing challenges for future studies on this topic. First, the use of chambers to estimate emissions from flowing waters may introduce a positive bias to our emissions estimates (Lorke et al., 2015). We acknowledge that fixed chambers may alter turbulent outgassing, thus adding uncertainty to our estimates. Prior studies have tried overcome this using options that were not well suited to first order streams at Coweeta because of their geomorphology, such as tapered chamber ends (Crawford et al., 2013) or freely floating chambers (Looman et al., 2017). Our k_{600} calculations from paired flux and dissolved gas measurements are not higher than we would expect from headwater streams (Raymond et al., 2012), which would be the case if the chamber was exerting a strong bias on emissions. k_{600} values were at the high end but within range of those published for vernal pools (Farr, 2014). Some of our fluxes estimated indirectly using calculated k_{600} values were the highest (for CO₂) or among the highest (for CH₄), of all our flux estimates, especially in the vernal pool patches (Figure S1). However, none of those higher estimates were far from directly measured flux within a similar patch. Finally, prioritizing using high spatial resolution measurements to inform patch and corridor greenhouse gas emissions estimates across a few forested headwater catchments, we were unable to delve more into temporal changes to linkages among different patches within corridors.

We found that the stream corridor structure had a strong influence on carbon emissions, as patch types indicated interesting linkages between channel features or hydrologic conditions. We measured heterogeneous stream emissions over small spatial scales, which improves our understanding of how carbon enters, moves through, and exits ecosystems. Higher resolution sampling is impractical in many studies, but where possible it can shed light on unique control points for biogeochemical activity over changing terrain and hydrology (Crawford, Stanley, et al., 2017; Horgby et al., 2019). Connectivity between patches will affect carbon emissions and export by distributing or restricting different sources of dissolved gases and organic matter. The presence of a riparian vernal pool influenced carbon emissions from a stream corridor, supporting the need to better integrate biogeochemical measurements across ecosystem types to advance our perspectives on carbon fluxes and fate as materials move within and beyond ecosystem boundaries. To assess carbon flux from all surface water in a large basin, knowing that the basin contains some subwatersheds with ephemeral vernal pools and intermittent streams, we would be remiss to only sample stream surface water near a catchment outlet. Without searching for patterns in terrestrial-riparian-aquatic connectivity and carbon flux, we will not be able to fully tackle questions around the global freshwater carbon budget.

Data Availability Statement

The CO₂ and CH₄ flux, CO₂ and CH₄ discrete concentration, and CO₂ sensor data used to characterize patch CO₂ and CH₄ dynamics in the study are available at Hydroshare via <https://doi.org/10.4211/hs.ab2b33f27b-3b4a0ca9a8ce4b8936753f> (Bretz et al., 2021).

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