Partitioning Inorganic Carbon Fluxes from Paired O₂ - CO₂ Gas Measurements in a Neotropical Headwater Stream, Costa Rica

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Abstract

The role of rivers and streams in the global carbon (C) cycle remains unconstrained, especially in headwater streams where CO_2 evasion (F_{CO_2}) to the atmosphere is high. Stream C cycling is understudied in the tropics compared to temperate streams, and tropical streams may have among the highest F_{CO_2} due to higher temperatures, continuous organic matter inputs, and high respiration rates both in-stream and in surrounding soils. In this paper, we present paired in-stream O_2 and CO_2 sensor data from a headwater stream in a lowland rainforest in Costa Rica to explore temporal variability in ecosystem processes. Further, we estimate groundwater CO_2 inputs (GW_{CO_2}) from riparian well CO_2 measurements and assess all fluxes to examine the relative contributions of sinks and sources of dissolved inorganic C (DIC) to a headwater stream. Paired O_2 - CO_2 data reveal stream CO_2 supersaturation driven by groundwater CO_2 inputs and large in-stream production of CO_2 . Areal fluxes in our study reach show F_{CO_2} is supported by both GW_{CO_2} inputs and in-stream metabolism and the seasonality in GW_{CO_2} reflects the hydrology of the site. Using a mass balance approach, we show F_{CO_2} is the dominant loss of DIC from the stream, greater than dissolved exports, and is sustained by both internal production of DIC and terrestrial inputs of DIC. Our results underscore the importance of tropical headwater streams as large contributors of greenhouse gases to the atmosphere among inland waters and show of this C derives from both in-stream and terrestrial sources.

1. Introduction

Inland waters play an important role in the global carbon (C) cycle and estimates of C fluxes between inland waters, the atmosphere, and terrestrial ecosystems are being revised at a rapid rate (Cole et al. 2007; Raymond et al. 2013; Drake et al. 2018; Tank et al. 2018). Streams, wetlands, and lakes transform, export, and store terrestrial C prior to delivery downstream to the ocean (Cole et al. 2007) and contribute CO_2 to the atmosphere (Battin et al. 2009). These processes are particularly important in headwaters streams, which comprise 79% of stream length (Colvin et al. 2019) and disproportionately contribute to evasion of CO_2 to the atmosphere on an areal basis (Raymond et al. 2013; Borges et al. 2019). However, these findings represent the synthesis from predominantly temperate systems, whereas tropical streams have received less study (Aufdenkampe et al. 2011; Oviedo-Vargas et al. 2015). As a result of higher year-round temperatures, high and continuous organic matter inputs, and drain soils with high respiration rates, tropical streams are likely to be hotspots of greenhouse gas emissions and fluxes (Borges et al. 2019). In-stream production of CO_2 from processing of organic matter can further contribute to high CO_2 fluxes (Richey et al. 2002; Mayorga et al. 2005; Hotchkiss et al. 2015).

Streams are generally supersaturated with respect to atmospheric CO_2 (Wetzel and Likens 2000), reflecting large fluxes of CO_2 into headwater streams of both terrestrially derived and internally produced CO_2 . Terrestrially derived CO_2 originates from soil respiration and CO_2 -rich geologic formations and is transported to headwaters via overland, subsurface, and groundwater flow. In contrast, CO_2 from internal processes is the result of respiration by in-stream heterotrophs. In headwater streams, the influence of

terrestrially derived CO₂ is typically greater than internal production and decreases in importance in larger streams and rivers (Hotchkiss et al. 2015). Losses of CO₂ from streams include evasion to the atmosphere, uptake through photosynthesis, and hydrologic export downstream. Evasion of CO₂ from freshwaters is a large flux of C sometimes unaccounted for in terrestrial budgets (Genereux et al. 2013) and is important at global scales (Raymond et al. 2013). Hydrologic export of dissolved inorganic carbon (DIC) includes all forms of C in equilibrium with the carbonate system, as aqueous CO₂, H₂CO₃, HCO₃⁻, and CO₃²⁻, which speciate according to pH (Stumm and Morgan 1996). High concentrations of CO₂ may reduce pH by an amount that depends on the buffering capacity of the water (Wetzel and Likens 2000; Small et al. 2012) and accelerate dissolution of carbonate minerals (Stoddard et al. 1999).

Advances in sensor technology allow measurement of CO₂ and O₂ at high frequency in freshwaters (Johnson et al. 2010), permitting estimation of fluxes of these gases at different hydrologic conditions and as drivers of stream physicochemistry. Results from discrete sampling of evasion and lateral inputs of CO₂ reveal important aspects of underlying processes and estimates of upscaled fluxes (Oviedo-Vargas et al. 2015). Aquatic sensors allow partitioning into sources and sinks at higher frequency and under conditions hard to capture using discrete sampling (e.g. floods). Further, coupling net ecosystem productivity (NEP) data with CO₂ sensor data allows for finer parsing of CO₂, variability across the hydrologic conditions, and evaluate processes that affect concentrations of both gases together (e.g. gas exchange, respiration) and separately (e.g. anaerobic respiration) (Vachon et al. 2020). Previous studies spanning various stream types across the continental US identified temporal patterns in headwater stream CO₂, from diel to annual and influenced by biology, physics, and hydrology (Crawford 2017). While combining CO₂ and O₂ sensor data in headwater streams to partition and account for various sources and sinks has been applied in Arctic and temperate streams (Lupon et al. 2019; Rocher-Ros et al. 2019), these methods have not been applied in tropical streams.

In this paper, we present the results of continuous deployment of O₂ and CO₂ sensors in a lowland Neotropical rainforest headwater stream in La Selva Biological Station, Costa Rica. We supplemented in stream sensors with a riparian well CO₂ sensor to measure groundwater CO₂ concentration and from that, calculate groundwater CO₂ inputs (GW_{CO2}). We combined sensor data to estimate CO₂ fluxes into and out of a 75-m study reach, including hydrologic export, NEP using O₂ data, evasion, and groundwater inputs. The hourly measurement frequency for six months allowed capturing short (e.g. rainfall) and long-term (e.g. seasonal) dynamics of C fluxes. We hypothesized that: 1) CO₂ would be supersaturated and O₂ undersaturated with respect to atmospheric equilibrium and the variation in paired gas concentration over time would reflect inputs from groundwater; 2) all C fluxes would increase during the wet season; 3) CO₂ evasion would be a greater than hydrologic export of C via stream flow; 4) discharge would drive increases in areal CO₂ fluxes; and 5) higher fluxes of GW_{CO2} would decrease stream pH.

2. Methods

2.1. Site description

La Selva Biological Station, Costa Rica (LSBS), is a 1600 ha tropical wet forest reserve, with elevation ranging from 22 to 146 meters above sea level (Fig 1). LSBS is located at the transition from the upland foothills of the Cordillera Central of Costa Rica and the Caribbean lowlands, and is the lowland terminus of the altitudinal transect in the Braulio Carrillo National Park (Fig 1). Mean annual rainfall from is 4300 mm, with dry season January to April and wet season July to December (Sanford et al., 1994).

We focused on the lower 75 m reach of the Taconazo stream (10.432, -84.013) to partition and quantify CO_2 input (upstream input, NEP, and GW_{CO_2}) and output (F_{CO_2} , downstream hydrologic export) fluxes. The Taconazo watershed area is 0.28 km², all of which is forested with a closed canopy (Table 1). The Taconazo is a low solute stream at LSBS, with long-term (1997 - 2015) mean water temperature of 25.1 °C, pH of 5.5, discharge of 0.06 m³ s⁻¹, and NO_3^- and SRP of 192.4 µg L⁻¹ and 4.9 µg L⁻¹, respectively (Ganong et al. 2015). The Taconazo has received significant study as a model headwater lowland tropical stream. Numerous studies from the Taconazo have contributed to better understand of the hydrology (Genereux et al. 2005; Genereux and Jordan 2006), biogeochemistry (Small et al. 2012; Oviedo-Vargas et al. 2015; Osburn et al. 2018), and ecology (Ardón et al., 2006; Ramírez et al., 2003; Rosemond et al., 2002) of tropical lowland headwater streams.

2.2. Data collection

We collected stream data from April 1, 2013 - September 30, 2013. Discharge (m³ s⁻¹) was continuously measured from the V-notch weir constructed near the outflow of the Taconazo; further descriptions of the weir in Zanon et al. (2014). Rainfall (mm) was collected from the LSBS weather station, located ~900 m from the Taconazo. Meteorological data are available at:

<https://archive.tropicalstudies.org/meteoro/default.php?pestacion=201>.

Groundwater discharge into the 75 m study reach was measured using conservative tracer injections to the stream. In the dry season (April), groundwater flux into the reach was 20% of total discharge at the end of the reach (Oviedo-Vargas et al. 2015), compared to the wet season (May-September) flux of 9% (Oviedo-Vargas et al. 2015, Ardón et al. 2013). For the dry and wet season, we multiplied discharge by the respective percentages as an estimate of groundwater discharge (Q_{GW}). To calculate discharge into the upstream end of the study reach (Q_u), the groundwater discharge in the reach was subtracted from stream discharge measured at the end of the study reach (Q_d).

A YSI 600xlm multiprobe sonde was secured 5 cm above the stream bottom in a PVC tube with holes drilled to allow for exchange of stream water. The multiprobe continuously measured temperature (°C), pH, and DO (mg L⁻¹ and %-saturation) at hourly intervals. The sonde was retrieved every two weeks for recalibration and to clean fouling on the sensor heads. Partial pressure of CO_2 (ppmv) was measured using a Vaisala GMT221 infrared gas analyzer (IRGA) in the stream and in a riparian well. The sensors

were prepared for submerged deployment as described in Johnson et al. (2010) and $p\text{CO}_2$ was logged hourly using a Campbell CR1000 datalogger. $p\text{CO}_2$ data were processed according to Johnson et al. (2010) for depth and temperature. We removed data from all sensors when the water level fell below the height of the sonde (e.g. conductivity < 0.005, DO near air saturation). Sensor data underwent further QAQC following the guidance of Taylor and Loescher (2013) and using the datacleanr R package (Hurley 2021).

2.3. Evaluating aqueous concentrations of CO_2 and O_2

We evaluated the departure of stream CO_2 and O_2 concentrations relative to concentrations expected at atmospheric equilibrium, and the magnitude of gas departure over time. Departure of O_2 and CO_2 from equilibrium with the atmosphere in freshwaters is mediated by biochemical reactions that directly link O_2 and CO_2 (e.g. aerobic metabolism), water temperature, bicarbonate chemistry, and gas exchange (Vachon et al. 2020). We calculated CO_2 departure as the difference of measured aqueous concentration ($[\text{CO}_2]_{\text{aq}}$) minus the concentration at atmospheric equilibrium at 400 ppmv ($[\text{CO}_2]_{\text{sat}}$) using a temperature-corrected Henry's Law constant. O_2 departure was calculated as the difference between in-stream concentration minus the concentration at saturation which is calculated as a function of temperature and barometric pressure, following the outline in Hall and Hotchkiss (2017) and detailed below.

Paired O_2 and CO_2 departure were plotted as a data cloud, O_2 departure vs. CO_2 departure. To evaluate movement of the cloud over time, we estimated 95% confidence interval ellipses for each month of data collection using the ellipse v0.4.2 R package (Murdoch and Chow 2020). In each ellipse, we calculated the: 1) centroid, which indicates the location in Cartesian space for both O_2 and CO_2 ; 2) $1/[\text{slope}]$ through each ellipse, which informs the efficiency of metabolism between O_2 and CO_2 , interpreted as the moles of CO_2 produced per moles of O_2 consumed through ecosystem respiration. See Vachon et al. (2020) for more details on these metrics.

To examine the role of individual rainfall events (2067 mm over 180 days) on $p\text{CO}_2$, we selected three storm events: one event from the dry season (April), early wet season (June), and late wet season (August). For the three events, we examined the hysteresis response of $p\text{CO}_2$ to discharge. For each event, we selected data 1 hour prior to the rising limb, through the peak in discharge, and for 5 hours following return to pre-storm discharge and before the next rising limb in the hydrograph (Evans and Davies 1998; Dinsmore and Billett 2008). We evaluated each hysteresis response for diagnostics describing the solute-discharge rotation (clockwise vs. counterclockwise vs. 'figure 8') and trend (positive vs. negative) (Evans and Davies 1998).

2.4. CO_2 flux calculations and reach scale DIC mass balance

Our data collection allowed for independent calculation of CO₂ input and output fluxes in the study reach. We calculated aqueous CO₂ from the in-stream (see section above) and riparian well ([CO₂]_{GW}) stations from *p*CO₂ data using the temperature dependent Henry's Law constant from Plummer and Busenberg (1982). Stream CO₂ at saturation ([CO₂]_{sat}) was determined using the same method, taking 400 ppm as the atmospheric CO₂ concentration (Rocher-Ros et al. 2019).

We compared sensor estimates of DIC to DIC estimates from samples of stream water. Samples were collected in 10 mL syringes and 4 mL of water was injected into an inverted sealed serum vial with a 22-gauge needle and 0.45 µm pore filter. Samples were equilibrated on a shaker table, and 250 µL headspace was removed and *p*CO₂ analyzed on an SRI Instruments gas chromatograph (Las Vegas, Nevada, USA). Conversions from *p*CO₂ to DIC were calculated as described in the supplementary file for sensor data. We matched the dates of syringe samples with sensor derived estimates and compared the two methods using the Student's t-test.

We defined CO₂ inputs to the study reach as the groundwater CO₂ flux (GW_{CO2}) and in-stream net ecosystem production (NEP). Groundwater CO₂ flux was calculated as

$$GW_{CO_2} = \frac{Q_{GW}}{SA} * [CO_2]_{well} \quad 1$$

Where SA is the benthic area of the stream and the flux units are mol C m⁻² h⁻¹

CO₂ inputs from in-stream aerobic metabolism was estimated as hourly NEP using the instantaneous direct metabolism method outlined in Hall and Hotchkiss (2017). Briefly, NEP was estimated from the volumetric O₂ mass balance equation:

$$NEP_i = \left(\frac{O_i - O_{i-\Delta t}}{\Delta t} - K_O(O_{sat,i} - O_i) \right) * \bar{z} \quad 2$$

Where NEP_i is hourly instantaneous metabolism (mol O₂ m⁻² h⁻¹), O_i is the O₂ concentration at each timepoint (mol m⁻³), O_{sat,i} is the concentration of O₂ at saturation for the same timepoint (mol m⁻³), *z* is stream depth (m), and K_O is the gas exchange coefficient for O₂ (h⁻¹). We converted K_O from K_{CO2} (see equation 3) via Schmidt scaling (Raymond et al. 2012). NEP was converted to mol C m⁻² h⁻¹ assuming a 1:1 respiratory quotient between O₂ and CO₂ (Rocher-Ros et al. 2019). We selected the direct metabolism method for determining NEP because the lack of a diel O₂ signal (Fig S1) and relatively high reaeration make the Taconazo ill-suited to alternative stream metabolism methods (Appling et al. 2018). Further, the direct method allows for estimation of NEP at finer temporal compared to alternative approaches, which are resolved at the daily scale.

CO₂ output as areal CO₂ evasion (F_{CO_2} , mol C per stream surface area per hour, m⁻² h⁻¹) was calculated as

$$F_{CO_2} = ([CO_2]_{aq} - [CO_2]_{sat}) * K_{CO_2} * \bar{z} \quad 3$$

Where K_{CO_2} is the dry (1.13 h⁻¹) or wet season (0.43 h⁻¹) gas exchange coefficient reported in Oviedo-Vargas et al. (2015), and $\bar{z}$ is depth in meters measured at the weir.

We conducted a volumetric mass balance in terms of DIC at the reach scale to compare reach scale estimates with watershed scale hydrologic inputs (upstream inputs and downstream export). The mass balance scales the fluxes calculated in equations 1-3 from mol C m⁻² h⁻¹ to reach as mol DIC h⁻¹; conversion of CO₂ to DIC are detailed in the supplementary file. Upstream DIC inputs to the study reach were calculated as the product of upstream discharge and [DIC] and upstream discharge was as the difference of downstream discharge and groundwater flux in the reach, which is an assumption supported in previous work (Ardón et al. 2013, Oviedo-Vargas et al. 2015). Thus, the full mass balance is:

$$\frac{dC}{dt} = [((Q_d - Q_{GW}) * C_d) + (Q_{GW} * C_{GW}) + (NEP(Lw\bar{z}))] - [(F_{CO_2}(Lw) + Q_d C_d)] \quad 4$$

Where C is DIC (mol m⁻³), Q is discharge (m³ h⁻¹), L is the reach length (75 m), w is wetted width (1.5 m in the dry season, 2.8 m in the wet season), z is depth (m) measured at the weir, NEP is volumetric net ecosystem production (mol DIC m⁻³ h⁻¹) and subscripts d, u, and GW refer to downstream, upstream, and groundwater, respectively. We evaluated the mass balance through the $dDIC/dt$ term. If all relevant fluxes are accounted for, the change in should average zero, representing DIC inputs and outputs in balance with no net change in C storage in the reach.

We aggregated fluxes from the DIC mass balance to daily rates to evaluate the correlation with daily rainfall and the extent groundwater flux could predict stream pH. Hourly fluxes were aggregated to daily rates as the sum of hourly fluxes, daily rainfall the sum of hourly rainfall, and pH as mean daily pH. To evaluate univariate control of CO₂ fluxes by discharge, we used the Kendall rank correlation, τ , on daily aggregated data. We evaluated the relationship of groundwater inputs of CO₂ as a driver of stream acidification events in the Taconazo. All analysis, statistics, and figures were made in R v4.0.3 (R Core Team 2020).

3. Results

3.1. Stream data

Total rainfall during the 180-day monitoring period was 2067 mm, with median daily rain of 2.29 mm (range: 0 – 107 mm) and 49 days with no rainfall recorded (Fig 2, a). April had the lowest rainfall (104.1 mm) and June had the most rainfall (498.6 mm). Median hourly stream discharge was $0.004 \text{ m}^3 \text{ s}^{-1}$ (0 – $1.378 \text{ m}^3 \text{ s}^{-1}$ range). Median discharge was lowest in April ($0.0002 \text{ m}^3 \text{ s}^{-1}$) and greatest in July ($0.0160 \text{ m}^3 \text{ s}^{-1}$). Median estimated groundwater flux into the reach was $0.0003 \text{ m}^3 \text{ s}^{-1}$ (0 – $0.0346 \text{ m}^3 \text{ s}^{-1}$ range) (Fig 2, b). Median $p\text{CO}_2$ in the stream was 6343.6 ppmv (range 773 – 11994 ppmv), lower than that measured in the riparian well (median $p\text{CO}_2$ 46924 ppmv, range 28663 – 48683 ppmv). Over the monitoring period, 14% of hourly $p\text{CO}_2$ measurements were missed in the stream, the largest missing section corresponding with the highest flows in late July and early August (Fig 2, d). In the riparian well, 27% of hourly measurements were missing, including the same period missing from the stream time-series and a period in May, during the transition from dry to wet season (Fig 2, e). Estimates of DIC from both discrete sampling (mean $0.23 \pm 0.06 \text{ mmol DIC L}^{-1}$) and from the sensor (mean = $0.25 \pm 0.04 \text{ mmol DIC L}^{-1}$) were similar ($p = 0.34$).

3.2 Gas dynamics and CO_2 hysteresis

In departure space, all data points show strong CO_2 super-saturation and O_2 undersaturation (Fig 3). CO_2 departure was ~6.6-times greater than O_2 departure, on average. Ellipse centroid location varied little over time. The value of $1/[\text{slope}]$ was greatest in September (467.9) and lowest in August (0.7). The general position of the cloud away from the 1:1 line indicates aerobic metabolic processes are not responsible for controlling CO_2 or O_2 , and the higher concentration of CO_2 than O_2 suggests anaerobic production of CO_2 or external inputs of CO_2 .

There is little evidence of hysteresis between $p\text{CO}_2$ and discharge in the three storm events we examined. In the dry season, $p\text{CO}_2$ varies little across the rise in discharge, though during the falling limb, there is slight ‘figure 8’ rotation (Fig 4, a). Similarly, $p\text{CO}_2$ varied little preceding and during the wet season events, while decreasing during the falling limb before returning to pre-storm concentration (Fig 4, b). In the late wet season, $p\text{CO}_2$ stays relatively constant during the rising limb, before oscillating during the falling limb (Fig 4, c). Of note, during the early wet season event, overall $p\text{CO}_2$ was greater than during the dry and late wet season events, and peak event discharge during the dry season ($0.01 \text{ m}^3 \text{ s}^{-1}$) was less than the early ($0.08 \text{ m}^3 \text{ s}^{-1}$) and late ($0.08 \text{ m}^3 \text{ s}^{-1}$) wet season events.

3.3. Areal CO_2 fluxes and DIC mass balance

The relationship between mean hourly CO_2 inputs and evasion to the atmosphere varied temporally. GW_{CO_2} (mean $1.39 \text{ mmol C m}^{-2} \text{ h}^{-1}$) showed strong monthly variation, with lower magnitudes in April and

May compared to June and July (Fig 5, a). The other input, NEP ($3.16 \text{ mmol C m}^{-2} \text{ h}^{-1}$), showed little variation over time (Fig 5, b). Evasion showed little temporal variation (mean $20.5 \text{ mmol C m}^{-2} \text{ h}^{-1}$).

Reach scale mass balance inputs reveal shifts in dominant contributions over time. The input with least temporal variation was NEP (mean $0.75 \text{ mol DIC h}^{-1}$), and was greater, on average, than upstream longitudinal inputs (mean $0.40 \text{ mol DIC h}^{-1}$) and groundwater ($0.31 \text{ mol DIC h}^{-1}$) (Fig 6, a). Upstream DIC and groundwater fluxes each reflect the seasonal hydrology of the stream, with lower fluxes in April, and greater values during the remaining wet season. DIC outputs at the reach scale were predominately to the atmosphere rather than hydrologic export (Fig 6, b). Mean evasion ($4.8 \text{ mol DIC h}^{-1}$) was ~ 11 times greater, on average, than hydrologic export (mean $0.44 \text{ mol DIC h}^{-1}$), and did not reflect changes in seasonal hydrology. The mass balance reveals that the Taconazo study reach is a net source of DIC (Fig 6, c). The central tendency of the mass balance near -4 suggests we accounted for major fluxes in the reach, but not centered at 0 suggests a discrepancy in this approach. Using the Kendall rank correlation statistic, τ , daily upstream DIC inputs and downstream outputs of DIC were significantly correlated with daily rainfall. In contrast, none of the upscaled areal fluxes were statistically correlated with rainfall.

Mean daily pH was decreased as GW_{CO_2} increased (Fig 7) ($F_{1,134} = 8.84$, $p = 0.06$, $R^2 < 0.01$). There were differences in pH response between months and seasons. In the dry season (April), mean daily pH fell to 4.50 at GW_{CO_2} of $0.01 \text{ mol DIC d}^{-1}$. During the peak of the wet season (July), GW_{CO_2} was $>0.1 \text{ mol DIC d}^{-1}$ and corresponded to a mean daily pH of 5.0.

4. Discussion

We showed that an in-stream stream and well sensor approach can be used to estimate inputs of terrestrial C into streams via groundwater and to evaluate the relative contribution of the different inputs and outputs in a stream DIC budget. Further, we showed that CO_2 fluxes responded seasonally to changes in rainfall. We found evasion of CO_2 to be a major loss of C from the Taconazo, underscoring the importance of considering fluxes from headwater streams in complete C assessments and budgets.

4.1. $p\text{CO}_2$ and O_2 variability

$p\text{CO}_2$ values measured in the Taconazo were high relative to similarly sized streams. Compared to a monitoring study across headwater streams in North America, Taconazo $p\text{CO}_2$ was higher than 6 of the 7 streams monitored, only less than a site in a southern hardwood forest and greater than a highland tropical stream in Puerto Rico (Crawford et al. 2017). We observed little diel variability in $p\text{CO}_2$ or O_2 (Fig S1), indicating gross primary productivity (GPP) is low in the Taconazo, and supported by the NEP estimates $> 0 \text{ mol C m}^{-2} \text{ h}^{-1}$ (Fig 3). In addition, the paired O_2 - CO_2 cloud (Fig 3) is located far from the 1:1 line for all time points, suggesting that aerobic metabolism is not a dominant process in the Taconazo and is not responsible for driving O_2 and $p\text{CO}_2$. In tundra headwater streams, the location of

the $\text{CO}_2\text{-O}_2$ departure cloud was closer to the 1:-1 line and reflected the greater influence of in-stream NEP on F_{CO_2} (Rocher-Ros et al. 2019).

The monitoring period included one month of the dry season with the remaining five months during the wet season, following the seasonality reported at LSBS (Sanford et al. 1994). The transition from dry to wet season is reflected by the increased rainfall in mid-May. The dry to wet transition coincides with an increase in stream $p\text{CO}_2$. During the wet season, there was greater variability in both stream $p\text{CO}_2$ and well CO_2 . The higher $p\text{CO}_2$ in the wet season reflects higher GW_{CO_2} flux corresponding to higher discharge and groundwater flux into the Taconazo and lower fluxes in the late wet season, following the peak of the wet season in July and August. Throughout the study period, some storm events resulted in decreases in $p\text{CO}_2$ (Fig 4, b), but was not a consistent pattern. The lack of consistent hysteresis between $p\text{CO}_2$ and discharge is perhaps limited by the events we examined, but a clockwise hysteresis is present during larger storms with greater turbulence that increases gas exchange rates.

4.2 Variability of areal and reach-scale fluxes

Among the areal fluxes, F_{CO_2} was greater than the input fluxes NEP and GW_{CO_2} (Fig 5). GW_{CO_2} showed strong seasonal variability, reflecting shifts in rainfall and discharge in the Taconazo (Fig 5, a), whereas NEP was similar in magnitude across the six-month period (Fig 6, b). Surprisingly, GW_{CO_2} and NEP values are similar in magnitude, contrasting with the gas departure data (Fig 3). We expected, as is characteristic in headwater streams, for external C contributions (GW_{CO_2}) to exceed in-stream production (NEP) (Hotchkiss et al. 2015). While the gas departure data suggest that aerobic processes are not responsible for mediating O_2 and CO_2 concentrations in the stream, gas flux data (Fig 5) suggests that NEP and GW_{CO_2} are similar C inputs in the lower Taconazo. This discrepancy could be explained by the independent calculation of each flux. First, the hydrology of groundwater discharge varies spatially within the study reach, and may exhibit a temporal lag between rainfall and discharging into the stream, and thus underestimates of GW_{CO_2} . Second, NEP is difficult to estimate with low diel O_2 variation (Appling et al. 2018). Third, estimates of evasion are likely underestimated due to the limited gas exchange data measured during low flows and missing high discharge events.

CO_2 evasion showed little temporal variability (Fig 6, b). We attribute the lack of variability to the sustained high $p\text{CO}_2$ relative to the atmosphere. Theory predicts gas exchange to increase with turbulence and geomorphological parameters, such as depth and velocity, and therefore with discharge (Raymond et al. 2012; Ulseth et al. 2019). Since our results are based on only two estimates of gas exchange estimates, the potential influence of discharge-driven temporal variation of gas exchange on evasion may be substantially reduced in our estimates. Streams like the Taconazo, with relatively high gas exchange rates and little diel O_2 variation are ill-suited to use inverse modeling outputs (Appling et al. 2018) or night-time regression to estimate gas exchange, using direct tracer injections of gases is an important method (Raymond et al. 2012). Our gas exchange rates were measured during low flows,

missing high discharge events, and there may be finer spatial scale areas within the study reach that have higher evasion but are masked in our one sensor station approach (Schneider et al. 2020). Our mean daily F_{CO_2} estimate ($4.6 \text{ g C m}^{-2} \text{ d}^{-1}$) was within the range of discrete estimates from the same reach during the same year (dry 10.8 ± 4.8 , wet $7.2 \pm 3.6 \text{ g C m}^{-2} \text{ d}^{-1}$, Oviedo-Vargas et al. 2015) and was greater than the average of six Arctic streams ($1.6 \text{ g C m}^{-2} \text{ d}^{-1}$, Rocher-Ros et al. 2019).

At the reach scale, the mass balance reveals that F_{CO_2} was the dominant loss of DIC (Fig 6); this highlights the need for estimates of greenhouse gases from tropical inland waters, particularly from headwater streams (Cole et al. 2007, Raymond et al. 2013). Elevated F_{CO_2} compared to the dominant DIC inputs (Fig 5) also contributes to the reach being a source, as determined by the negatively skewed $d[\text{DIC}]/dt$ distribution (Fig 6, c), and the reach is perhaps a greater DIC source given the potential underestimation of F_{CO_2} . With little change in stream pCO_2 during storms (Fig 4), hydrologic exports of DIC follow short-term patterns and the seasonality in discharge. The mass balance deserves further scrutiny given the magnitude of the fluxes regulating DIC within the 75 m reach and the assumptions about [DIC] at the upstream and downstream ends of the reach.

4.3. Drivers of CO_2 fluxes

The location of the O_2 - CO_2 cloud represents CO_2 supersaturation and slight O_2 undersaturation, on average (Fig 3) and based on the predictions in Vachon et al. (2020), we conclude that groundwater CO_2 inputs are largely responsible between internal and external sources of CO_2 . However, the flux data suggest that NEP is a similarly sized contributor to DIC in the reach. The $1/[\text{slope}]$ for each monthly cloud (Table 2) suggests the ecosystem respiratory quotient, as mol CO_2 produced for mol of O_2 consumed in aerobic processes, are >1 (except August), further contributing to the supersaturation of CO_2 . We conclude that pCO_2 and the fluxes that affect pCO_2 in the Taconazo are mediated primarily by groundwater inputs (Figure S2), at broad timescales and is true for similar headwater streams in lowland tropical wet forests.

Rainfall explained variation in hydrologic inputs and exports in the mass balance, though not for GW_{CO_2} which has a hydrologic component in its calculation (Table 3). The lack of correlations for the other fluxes with rainfall is informative for headwater tropical streams. For F_{CO_2} , as previously discussed, the sustained high pCO_2 drives this flux and the influence of rainfall or storm events have little effect on pCO_2 . The sustained high pCO_2 measured in the riparian well explains why GW_{CO_2} is unaffected by rainfall. The lack of temporal variability in DO, and therefore NEP, indicate storm events are less important. Storm events do influence dissolved organic C (DOC) in the Taconazo (Osburn et al. 2018), which may contribute to increased respiration. Changes in the delivery of DOC that fuels in-stream respiration may be reflected in the differences in time of the $1/[\text{slope}]$ (Table 2) which reflects the ecosystem respiratory quotient, or conversion of O_2 into CO_2 during respiration at the ecosystem scale. In temperate streams with organic soils, rainfall events increased [DOC] and stimulated in-stream

ecosystem respiration (Demars 2019). It is unlikely primary productivity affects NEP in a measurable way. The dense canopy cover attenuates light at the stream bed and the food webs are fueled through detrital pathways (Rosemond et al. 2002), and there is little diel variation in DO (Fig S1), all suggesting photosynthetic uptake of C is small.

4.4. Influence on pH

Small et al. (2012) suggested that CO_2 from terrestrial sources enter streams with low solutes and reduce pH through carbonic acid creation, primarily during the early wet season in streams at La Selva. Our results provide some support for this hypothesis. We show GW_{CO_2} has a weak negative correlation with stream pH (Fig 7). In the late dry and early wet season (April – May, Fig 2), small inputs of GW_{CO_2} ($<10^{-3}$ mol DIC d^{-1}) can reduce mean daily pH to as low as 4.5 and these single day acidification events detract from the correlation ($R^2 = 0.06$), but are ecologically important. During the wet season (June onward), greater GW_{CO_2} reduce pH to between ~ 5 . The Taconazo has low alkalinity (<5 mg L^{-1} as CaCO_3 , unpub. data), therefore the acid neutralizing capacity is overcome by small inputs of CO_2 . CO_2 is supplemented by increased DOC during storm events (mean stormflow DOC = 2.25 mg L^{-1} , Ganong et al. 2015; Osburn et al. 2018) and redox reactions (e.g. iron oxidation) which can collectively reduce pH. During the wet season, DOC inputs to the Taconazo are disproportionately organic acids (Osburn et al. 2018) which have a pK_a that contributes to lower pH.

The lowest hourly pH measured during our study was 4.0 and is similar to lowest pH measured in the long-term record from the Taconazo, which occurred following the global El Niño Southern Oscillation event in 1997/98 (Small et al. 2012). During this event at LSBS, tree growth was decreased (Clark et al. 2003, 2010) and root mortality increased (Espeleta and Clark 2007). Small et al. (2012) hypothesize the stock of labile C in the soil increased and soil respiration causes high soil CO_2 (Schwendenmann and Veldkamp 2006). When soil moisture increases during the early wet season, soil CO_2 is quickly flushed from groundwater into streams. While acidification events are common in low solute headwater streams at La Selva, where pH ranges from 4 – 6 in the span of days, the negative effects on organisms and ecosystem processes are limited (Ganong 2015), though there is evidence of short term behavior modification in macroinvertebrates and fish (Ardón et al. 2013).

Conclusion

We deployed a trio of sensors, in a stream and in a riparian well, to independently estimate external and internal fluxes of CO_2 in a lowland headwater tropical stream. We found that values for terrestrial flux of CO_2 are similar to internal production as NEP. High F_{CO_2} was sustained and greater than hydrologic export of C. In a global synthesis of efflux from inland waters, both Cole et al. (2007) and Raymond et al. (2013) stress the importance of evasion estimates from headwater tropical streams, which exhibit higher reaeration velocities and higher $p\text{CO}_2$. We document sustained high $p\text{CO}_2$ leads to higher F_{CO_2} compared

to similar-sized headwater streams across the globe (Raymond et al. 2013). Our study provides estimates of globally relevant C fluxes from a stream type with disproportionate influence among inland waters and provides a sensor-based approach to independently estimate reach scale C fluxes.

Declarations

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Conflicts of interest

The authors have no relevant financial or non-financial interests to disclose.

Availability of data and material

Data, code, and supplementary material from this study can be accessed at https://github.com/nmarzolf91/Taconazo_CO2. Until acceptance of the paper, this repository is not publically available but all files in the repository will be uploaded during manuscript submission.

Code availability

Data, code, and supplementary material from this study can be accessed at https://github.com/nmarzolf91/Taconazo_CO2.

Author contributions

Conceptualization: N. Marzolf, C. Small, D. Oviedo-Vargas, C. Ganong, J. Duff, D. Genereux, M. Ardón; Methodology: N. Marzolf, C. Small, C. Ganong, D. Oviedo-Vargas, D. Genereux, M. Ardón; Formal analysis and investigation: N. Marzolf, C. Small, D. Oviedo-Vargas, D. Genereux, M. Ardón; Writing - original draft preparation: N. Marzolf, C. Small, M. Ardón; Writing - review and editing: all authors; Funding acquisition: M. Ardón, A. Ramírez, C. Pringle; Resources: C. Small, D. Oviedo-Vargas, D. Genereux, C. Ganong, M. Ardon; Supervision: M. Ardón, A. Ramírez, C. Pringle.

Ethics approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

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Tables

Table 1) Reach characteristics from the Taconazo and summary statistics for physicochemical data during the study period. High frequency data (temperature, DO, pH, $p\text{CO}_2$, and stream discharge) are presented as the median (range in parentheses) during the monitoring period.

Measurement (unit)	Value
Reach length (m)	75
¹ Mean reach width (m)	1.3
¹ Mean reach velocity (m s ⁻¹)	0.014
¹ Travel time (min)	82.5
Gradient (m m ⁻¹)	0.0024
Temperature (°C)	24.5 (21.2 – 29.6)
DO (mg L ⁻¹)	5.94 (0.26 – 8.32)
pH	5.32 (4.02 – 6.91)
pCO ₂ (ppmv)	6443.6 (773.8 – 11994)
² Stream Discharge (m ³ s ⁻¹)	0.017 (0 – 1.378)

¹ Measured in March 2013

² excludes backflooding events when the downstream Rio Puerto Viejo floods its tributaries, including the Taconazo (Zanon et al., 2014).

Table 2) Paired O₂ - CO₂ metrics for ellipses for each month of the monitoring period. Mean CO_{2-Dep} and O_{2-Dep} are mean monthly concentrations followed by standard deviation in parentheses. The 1/[slope] is the slope of the linear model fit through each months' data.

Month	Mean CO _{2-Dep} (SD)	Mean O _{2-Dep} (SD)	1/[Slope] (μM μM ⁻¹)
April	175.5 (46.6)	-48.6 (18.4)	20.5
May	204.2 (30.0)	-35.3 (14.2)	7.0
June	243.5 (33.9)	-32.0 (15.2)	12.1
July	207.7 (15.4)	-11.1 (5.2)	13.4
August	183.9 (14.9)	-30.0 (45.3)	0.7
September	221.2 (25.2)	-30.6 (12.8)	467.9
All Dates	204.3 (37.9)	-31.8 (24.8)	9.9

Table 3) Correlation of daily DIC fluxes with daily rainfall. Units for mass balance terms are mol C d⁻¹. Bold text indicates statistically significant correlations (*p* < 0.05).

	Mass Balance term (mol DIC d ⁻¹)	τ	<i>p</i> value
Inputs	GW _{CO2}	0.08	0.15
	NEP	-0.01	0.78
	DIC_u	0.16	<0.01
Outputs	DIC_d	0.16	<0.01
	F _{CO2}	0.05	0.37

Figures

Figure 1

Map of La Selva Biological Station filled with a 1 m digital elevation model. The Taconazo watershed (0.28 km²) is outlined in black and stream outflow is designated at the black circle.

Figure 2

a) Daily rainfall, b) hourly stream (black line) and groundwater (red line) discharge in the Taconazo, and hourly c) dissolved oxygen (mg L⁻¹) in the stream water, d) stream water pCO₂ (ppmv), and e) groundwater well pCO₂ (ppmv) in the riparian well. Asterisks (*) in panel “b” correspond to the storm events used to explore hysteresis.

Figure 3

Paired O₂ and CO₂ departure from atmospheric equilibrium. The color of the points indicate the month collected and richer colors reflect a higher density of points. The dashed line is the 1:-1.

Figure 4

Concentration - discharge plots of three storm events in the Taconazo during the a) dry season, b) early wet season (June), and c) late wet season (August). Point and line segment colors indicate the hour of the storm event, with dark colors showing early in the event and lighter later in the event.

Figure 5

Hourly areal CO₂ input fluxes on areal evasion, FCO_2 , in the Taconazo: a) Groundwater CO₂ flux and b) net ecosystem production. Dashed line is 1:1. Colors are daily fluxes colored by the month of the measurement. Note log₁₀ transformation and different range of the x-axes.

Figure 6

Reach scale mass DIC balance for the Taconazo. a) DIC inputs from groundwater (blue), net ecosystem production (yellow), and upstream inputs (grey). b) DIC losses from the reach as evasion (red) and hydrologic export downstream (light blue). c) Distribution of change in [DIC] term in equation 4.

Figure 7

Groundwater CO₂ flux as a driver of the mean stream pH. Grey line is line-of-best fit ($p < 0.01$) with shaded area the 95% confidence interval. Point color indicates the month and vertical bars for each point represent the pH daily standard deviation.

Supplementary Files

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