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ABSTRACT
São Paulo state is the largest sugarcane cultivation area in Brazil and the largest sugarcane producer in the world, yet the impact of sugarcane cultivation on carbon dynamics in tropical stream ecosystems remains poorly understood. We investigated CO_2 emissions and concentrations in streams draining sugarcane fields and native vegetation catchments to elucidate the influence of sugarcane cultivation on CO_2 dynamics in streams. Contrary to our hypothesis, streams from native vegetation catchments exhibited greater CO_2 emissions and concentrations than those from draining sugarcane fields. This result can be attributed to the soil respiration, which is higher in native vegetation catchments because of higher organic matter inputs. Our findings emphasize the significant role of tropical vegetation dynamics in shaping carbon dynamics in freshwater ecosystems and the connections between terrestrial and aquatic ecosystems in headwaters. Additionally, we observed higher CO_2 emissions during the summer, attributable to increased temperatures, streamflow, and terrestrial organic matter inputs in soils and streams. The variables influencing CO_2 concentrations were pH, conductivity, season, and methane concentration, highlighting the complex interplay of environmental factors. Future research should address critical gaps, including the effects of soil texture and liming on CO_2 dynamics, and the quantification of the contributions of methane oxidation to CO_2 emissions. Understanding these factors is vital for assessing the impact of sugarcane cultivation on freshwater carbon cycles, particularly in regions such as Brazil, which is a major contributor to global sugarcane production.

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Introduction

Headwater streams are important players in the processing and transporting the terrestrially derived organic carbon to carbon dioxide (CO_2) before it is delivered into the ocean (Hotchkiss et al. 2015, Peralta-Maraver et al. 2021). Approximately 72% of the total CO_2 emissions are derived from terrestrial carbon in streams and rivers (Hotchkiss et al. 2015), especially important in tropical streams because they are characterized by relatively high water temperatures and year-round litterfall dynamics (Taniwaki et al. 2017b). Because these factors can increase metabolic rates and CO_2 emissions (Cole et al. 2007), tropical freshwater ecosystems can disproportionally transform terrestrial-derived organic carbon to CO_2 when compared to their temperate counterparts (Ward et al. 2017). In addition, headwater streams can represent ~60% of the length of the entire drainage basin in the tropics (Taniwaki et al. 2018), reflecting their relevance for studies analyzing CO_2 emissions and their connections to land-use change and climate change.

Several different types of human impacts can alter CO_2 emissions and concentrations in tropical headwater streams by increasing organic carbon and nutrient loads into stream channels. In Brazil, most of these impacts are related to urbanization and agricultural practices (Mello et al. 2020). In São Paulo state, an important agricultural region in Brazil, one of the most common agricultural crops is sugarcane. The state is the largest producer in the country, and Brazil is the largest producer in the world (Cherubin et al. 2021, Zheng et al. 2022). Common practices particular to sugarcane production can alter carbon dynamics at the catchment scale, which will affect carbon dynamics

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in streams. For example, sugarcane straw is left on the soil to avoid soil erosion, and ethanol production residues (vinasse) are sprayed on the soil to increase soil fertility (do Carmo et al. 2013). Considering that the residues from these processes are carbon rich and can be carried into streams by runoff and carbon leaching, these agricultural practices likely alter the carbon dynamics in headwater streams and may increase CO_2 concentrations and emissions in these environments. In addition, sugarcane production, similar to that of large-scale agricultural crops, requires fertilization, especially nitrogen and phosphorus, which can reach freshwater ecosystems by runoff and subsurface runoff, increasing CO_2 emissions through alterations in the metabolic rates of methane-oxidizing bacterial communities (Saltarelli et al. 2018, Bonetti et al. 2022).

In addition to the effects of land-use changes and agricultural practices, seasonality can also interfere with CO_2 concentrations and emissions in tropical streams. In the tropics, litterfall inputs do not follow regular annual cycles as in temperate streams and show great variability in leaf breakdown rates because of the high diversity of vascular plants with different leaf characteristics (Wantzen et al. 2008), which affects carbon availability throughout the year. Many tropical streams are characterized by high energy inputs and fast rates of change in terms of hydrological characteristics, which affect how organic matter is processed in stream channels and groundwater (Wohl et al. 2012) and the gas transfer velocity for greenhouse gases produced in catchments and streams (Aho and Raymond 2019). In addition to these features, year-round temperatures are generally >15 °C (de Mello et al. 2018, Taniwaki et al. 2019), with water temperatures reaching >20 °C during the summer, which promotes decomposition and accelerates metabolic rates.

Considering the effects of seasonal changes and sugarcane cultivation on the soil and freshwater carbon cycles, we aimed to analyze whether sugarcane cultivation at the catchment scale affects CO_2 emissions and concentrations in headwater streams. Therefore, we tested the following hypotheses: (1) streams draining sugarcane fields would show greater CO_2 emissions and concentrations than native vegetation catchments because of the carbon inputs from sugarcane crops and fertilizer application; (2) CO_2 emissions and concentrations would be greater during the summer because of the increased temperature and streamflow; and (3) the most important variables controlling CO_2 concentrations would be related to dissolved carbon and total dissolved nitrogen concentrations in streams.

Methods

Study area

This study was conducted in the São Carlos, Itirapina, and Brotas municipalities in the state of São Paulo, southeastern Brazil. The climate is humid subtropical with hot summers (Kottek et al. 2006, Alvares et al. 2013). The average annual air temperature is 19.5 °C, with a maximum monthly average temperature of 21.9 °C in January and February and minimum monthly average temperature of 15.9 °C in July (Bere and Tundisi 2011). The total precipitation (30-year average for São Carlos municipality) is ~1500 mm yr^{-1}, with 35 mm of precipitation in the driest month (Aug) and 277 mm of precipitation in the wettest month (Dec).

The region, originally covered by the Cerrado (i.e., Brazilian woodland savannas), was extensively modified and is now predominantly covered by agriculture, with sugarcane as one of the most important crops (Machado et al. 2016, Finkler et al. 2018). The broader region of the central-north state of São Paulo, where our study sites are located, is the most important sugarcane-producing region in the world (Rudorff et al. 2010, Cherubin et al. 2021). Litterfall by native vegetation occurs year-round but is greater during the winter (~1 t ha^{-1}; Valenti et al. 2008). Sugarcane harvest in this region occurs between April and November, depending on the cropping system and sugarcane variety.

Six sandy/rocky-bottom headwater streams (first to second order) were selected based on the main land use in the catchment (Table 1, Fig. 1). Three headwater streams drained the sugarcane plantations, and the 3 other headwater streams drained native vegetation catchments (Cerrado vegetation). The "native vegetation 1" stream drained a municipal conservation unit inside of the Federal University of São Carlos, campus São Carlos. The "native vegetation 2" stream drained an area with an experimental grass field in addition to the native vegetation forest (Brazilian Agricultural Research Corporation – EMBRAPA). The "native vegetation 3" stream drained a catchment located in the Itirapina Ecological Station, an important conservation unit for Cerrado vegetation. Catchment drainage areas were determined by digital elevation models, and land use was classified based on satellite images from LANDSAT using ArcGIS software. These streams have been studied for methane dynamics (Taniwaki et al. 2022), and some have been previously studied in relation to nutrient uptake and stream metabolism (Dodds et al. 2017, Finkler et al. 2018, Saltarelli et al. 2018).

Three field campaigns with 3 replicate sampling dates within each campaign were conducted 3–6 and 11–14

Table 1. Main characteristics of the study streams and catchments in the state of São Paulo, southeastern Brazil. *65% of the native vegetation 2 catchment is occupied by grass and a laboratory, with little agricultural intervention.

Stream	Coordinate S	Coordinate W	Mean width (cm)	Mean depth (cm)	Catchment size (ha)	Native (%)	Sugarcane (%)
Sugarcane 1 (Fig. 1a)	21°56′50"	47°51′53"	83.7	7.2	62.8	8.2	86.0
Sugarcane 2 (Fig. 1b)	21°56′28"	47°51′30″	130.6	8.7	122.9	18.2	59.8
Sugarcane 3 (Fig. 1c)	22°09′41"	47°56′20"	117.3	13.1	104.9	11.7	88.3
Native vegetation 1 (Fig. 1d)	21°58′00"	47°50′33"	105.8	7.8	131.3	97.9	0
Native vegetation 2* (Fig. 1e)	21°58′46"	47°52′23"	69.1	18.8	267.0	31.7	0
Native vegetation 3 (Fig. 1f)	22°11′36"	47°53′52"	120.0	36.6	282.3	100	0

July (winter), 2–5 and 11–14 September (spring), and 13–20 December (summer) 2018. All samples were randomly collected among the streams between 0800h and 1600h. In each stream, a 60–100 m reach of the channel was selected to characterize the physicochemical properties of the stream water, to quantify the CO_2 concentrations of the stream water at 3 substations, and to conduct tracer experiments to quantify the gas exchange velocity across the air-atmosphere interface at 5 substations.

Physical and chemical characteristics of stream water

The physical and chemical characteristics of the stream water were measured at 3 sites within each stream, with 3 temporal replicates for each season. In situ physicochemical characterization of basic water quality parameters was conducted using a YSI Professional Plus handheld multiparameter meter (YSI, Yellow Springs, OH, USA) to determine dissolved oxygen (DO, mg L^{-1}), water temperature (Temp, °C), pH, electrical conductivity (EC, µS cm^{-1}), and oxidation-reduction potential (ORP, mV). Three water samples per stream were collected in 50 mL sterile RNase-/DNase-free polypropylene Falcon tubes for laboratory analysis and transported in refrigerated containers to the laboratory where total dissolved carbon, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC; detection limit of 4 µg L^{-1}), and total dissolved nitrogen (nitrogen compounds in filtered samples were oxidized at 720 °C – detection limit of 5 µg L^{-1}) were determined using a TOC-L

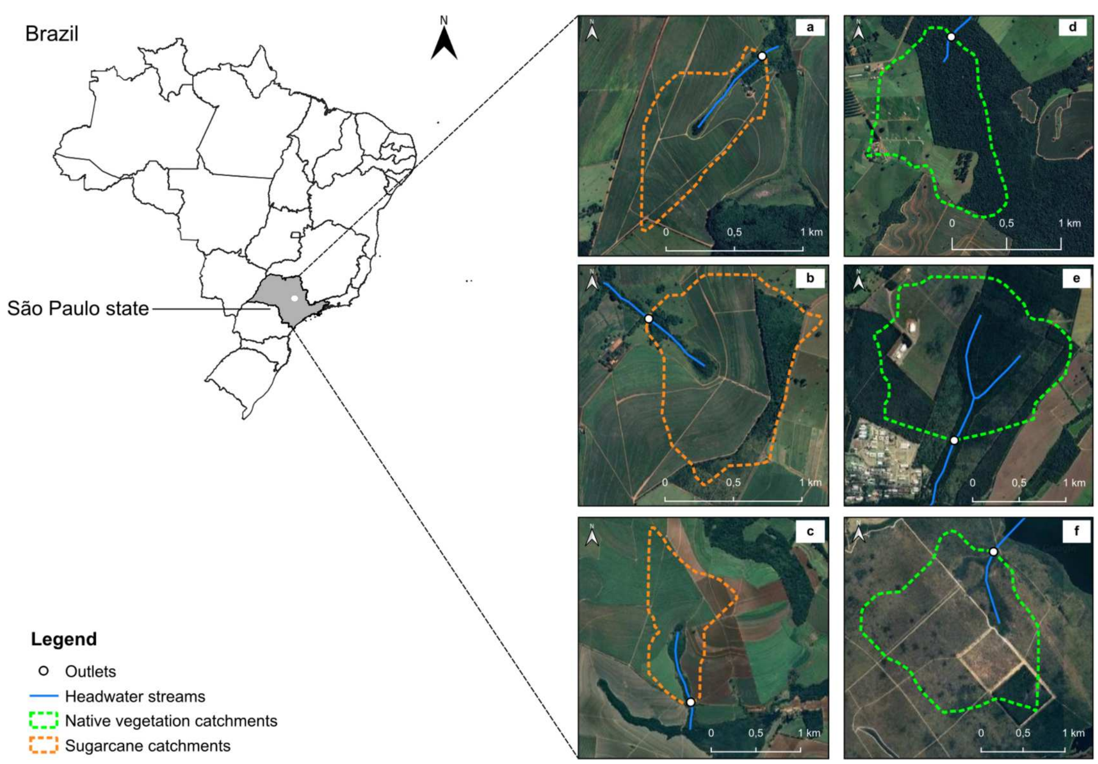

Figure 1. Location of the study catchments and their land use in São Paulo state, Brazil. (a–c) Catchments occupied by sugarcane cultivation (sugarcane 1, 2, and 3, respectively); (d–f) catchments occupied by native vegetation (native vegetation 1, 2, and 3, respectively).

Shimadzu TOC analyzer (Shimadzu Co., Kyoto, Japan) coupled with a TNM-L total nitrogen measuring unit (Shimadzu Co., Kyoto, Japan). The conservative tracer method was used to estimate the mean stream water velocity and streamflow (Stream Solute Workshop 1990). To achieve this, 60–100 m of stream length was selected, measured along the channel using a measuring tape. In each section, sodium chloride (NaCl) pulses were released upstream, and a YSI Professional Plus conductivity meter (YSI) was used to record the downstream conductivity every 15 s starting just prior to the addition of NaCl and continuing until the conductivity returned to the baseline conditions observed before the addition of NaCl (Webster and Valett 2007). All measurements were conducted after water sample collection at random times throughout the day, and as a result, diel cycles of streamflow were not considered.

CO_2 sampling and analysis

We collected 3 samples in each stream from a 60–100 m reach, with 3 temporal replicates in each season (spring, summer, and winter) using the headspace extraction technique (Schade et al. 2016). We were unable to collect samples from the "sugarcane 3" stream during spring and summer 2018 because of authorization issues to access the area. In the laboratory, 60 mL acid-washed syringes fitted with sealed 3-way stopcocks were filled with 30 mL of ultrapure nitrogen (5.0). In the field, 1 syringe was filled with 30 mL of stream water at each station. The stopcock was closed underwater to avoid any bubbles. Syringes were then shaken for 5 min to equilibrate gases between water and air, and the entire headspace gas was injected into a preevacuated gas-tight vial for CO_2 and methane analysis (Taniwaki et al. 2022). Gas samples were stored under positive pressure until analysis.

CO_2 analysis was carried out using a Shimadzu GC-2014 gas chromatograph equipped with an electron capture detector 63Ni (ECD, detection limit: 0.1 ppb) and a flame ionizer detector (FID, detection limit: 0.1 ppm) operating at 325 °C (Bowden et al. 1991) with a methanizer (operating at 380 °C). Gas concentrations were calculated by comparing peak areas for samples with standards (Scott-Marrin, Riverside, CA, USA – 1551, 1009, and 353 ppm) calibrated against standards prepared by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostic Laboratory (NOAA/CMDL, Boulder, CO, USA). The concentrations of CO_2 in the headspace were converted to partial pressures of CO_2 in the initial water samples using Bunsen solubility coefficients (Mulholland et al. 2004). CH_4 analyses were conducted in the same samples (methods for CH_4 analysis in Taniwaki et al. 2022).

CO_2 emissions

The CO_2 emission (F; equation 1) was calculated by multiplying the gas transfer velocity (K) by the difference between the measured dissolved concentration (C_w) and the predicted CO_2 concentration at equilibrium with the atmosphere (C_{eq}; Raymond et al. 2012, Beaulieu et al. 2016, Schade et al. 2016). The predicted CO_2 concentration was calculated using the partial pressure in the gas phase by the Bunsen solubility coefficient (equation 2; Weiss 1974):

$$F = K(Cw - Ceq), \quad (1)$$

where F is the CO_2 emission; K is the gas transfer velocity (m d^{-1}); and C_w – C_{eq} is the difference between the measured (μmol L^{-1}) and predicted (μmol L^{-1}) equilibrium concentrations.

$$Ceq = P_{CO_2} \times \beta_T \times P_{barometric}, \quad (2)$$

where Ceq is the equilibrium concentration of CO_2 (μmol L^{-1}); P_{CO2} is the partial pressure in the gas phase of CO_2 (in atm); β_T is the Bunsen solubility coefficient for CO_2 (Weiss 1974); and $P_{barometric}$ is the barometric pressure at each sampling site (atm).

Gas transfer velocities in all studied streams were estimated for 2 field campaigns (Jul and Dec, the dry and wet seasons) using the gas tracer method (Tsivoglou and Neal 1976, Raymond et al. 2012). Sulfur hexafluoride (SF_6) and NaCl were employed as conservative gas and solute tracers, respectively. SF_6 was continuously bubbled at an upstream station, and NaCl pulses were used to indicate the time needed for the stream channel to become saturated with SF_6. Once saturation was reached, gas samples were collected at 5 substations using previously described methods and analyzed using a Shimadzu GC-2014 gas chromatograph.

Equation 3 was used to estimate the downstream decrease in the SF_6 concentration (K_{SF6}) and the DO gas transfer velocity at the air–water interface (K_{DO}). We ran a linear regression between the Neperian logarithm of SF_6 concentration measured in the sampling stations and the total length of the reach (x) (Benson et al. 2014, Tromboni et al. 2017). The K_{DO} was obtained from each reach through the conversion factor proposed by Canale et al. (1995):

$$C_x = C_0 e^{-K_{SF6} t}, \quad (3)$$

where C_x is the SF_6 concentration at each sampling station (g m^{-3}); C_o is the initial SF_6 concentration (g m^{-3}) at the release point ($x = 0$ m); t is tracer residence time (d); and K_{SF6} is the gas transfer velocity for SF_6 (m d^{-1}).

The gas transfer velocity for CO_2 (K_{CO2}) was calculated by the Schmidt number, the ratio of the kinematic viscosity of water to the diffusion coefficient, used to calculate the gas transfer velocity of one gas from another (equation 4). K_{DO} was converted to K_{CO2} using published methods and protocols (Wanninkhof et al. 1990, Canale et al. 1995, Raymond et al. 2012):

$$\frac{K_{DO}}{K_{CO2}} = \left(\frac{Sc_{DO}}{Sc_{CO2}}\right)^{\frac{1}{2}}, \quad (4)$$

where, K_{DO} is the gas transfer velocity for DO (m d^{-1}), K_{CO2} is the gas transfer velocity for CO_2 (m d^{-1}), and Sc_{DO} and Sc_{CO2} are the Schmidt number for DO and CO_2, respectively. The equations for determining Sc_{DO} and Sc_{CO2} are available in Raymond et al. (2012).

Statistical analysis

We used descriptive statistics and nonparametric tests to compare the physical and chemical characteristics of stream water among different seasons and land uses after checking the lack of normality and homoscedasticity in several variables of our data. The differences among land uses were compared using Wilcoxon rank-sum test. For the comparisons between seasons, we used the Kruskal-Wallis test, and to compare the multiple pairs of means we applied the Dunn-Bonferroni post hoc test using the *FSA* package with $\alpha = 0.05$ (Ogle et al. 2020). To test the first and second predictions (i.e., that CO_2 concentrations and emissions are greater in the summer and in streams draining sugarcane catchments), we compared CO_2 emissions and concentrations in different seasons and across different land uses using Wilcoxon rank-sum and Kruskal-Wallis tests. All analyses were conducted in R software (R Core Team 2019).

To test our third prediction (i.e., that the most important variables controlling CO_2 concentrations are related to nutrient concentrations in streams), we first removed variables with multicollinearity through the variance inflation factor (VIF) test (O'Brien 2007) using the *caret* (Kuhn 2008) and *tidyverse* (Wickham et al. 2019) packages in R software (R Core Team 2019). In this step, the VIF test suggested removing total dissolved carbon from our analysis. After removing multicollinear variables, we used machine learning techniques and constructed a random forest model to identify and rank the main contributors for explaining the CO_2 concentrations in the studied streams (Breiman 2001, Cutler et al. 2007) through variable importance (VIMP), which represents the difference in out-of-bag prediction error before and after permutation (Ehrlinger 2014). The independent variables included in the model were pH, water conductivity, season, CH_4 concentrations, total dissolved nitrogen, dissolved oxygen, oxidation–reduction potential, water velocity, streamflow, water temperature, percentage of native vegetation in the catchment, DOC, and DIC using the *randomForestSRC* package (Ishwaran and Kogalur 2021) in R (R Core Team 2019).

Results

Physical and chemical characteristics of stream water

Stream water characteristics varied both seasonally and between the sugarcane (SG) and native vegetation (NV) catchments for most parameters (Table 2). Significant differences were observed between almost all parameters across land uses except for total dissolved carbon and streamflow. Streams draining sugarcane catchments had significantly greater values of water temperature (SG $\bar{x}$ 19.6 °C, NV $\bar{x}$ 17.9 °C), dissolved oxygen (SG $\bar{x}$ 7.89 mg L^{-1}; NV $\bar{x}$ 6.68 mg L^{-1}), conductivity (SG $\bar{x}$ 18.14 µS cm^{-1}, NV $\bar{x}$ 11.47 µS cm^{-1}), pH (SG $\bar{x}$ 6.09, NV $\bar{x}$ 5.01), water velocity (SG $\bar{x}$ 0.14 m s^{-1}, NV $\bar{x}$ 0.04 m s^{-1}), DIC (SG $\bar{x}$ 1.45 mg L^{-1}, NV $\bar{x}$ 0.95 mg L^{-1}) and total dissolved nitrogen (SG $\bar{x}$ 0.37 mg L^{-1}, NV $\bar{x}$ 0.13 mg L^{-1}). The parameters significantly lower in streams draining sugarcane catchments were oxidation–reduction potential (SG $\bar{x}$ 418 mV, NV $\bar{x}$ 526 mV) and DOC (SG $\bar{x}$ 0.52 mg L^{-1}, NV $\bar{x}$ 1.29 mg L^{-1}). The DOC concentrations were below global average concentrations of 10.4 mg L^{-1} (Liu and Wang 2022). The DIC concentrations were also below global average concentrations of ~60 mg L^{-1} (Cole and Prairie 2024).

In relation to the seasonal characteristics, the streams did not vary in relation to water velocity, DOC, total dissolved carbon, or total dissolved nitrogen. Other parameters were significantly different, mostly during the summer, except for dissolved oxygen, which was higher during the winter.

Land-use and seasonal effects on CO_2 emissions and concentrations

Streams draining native vegetation catchments showed greater CO_2 concentrations and emissions than did streams draining sugarcane fields ($p < 0.05$; Fig. 2a–b). The median (standard deviation) CO_2 concentration was 285 (109) µmol L^{-1} for streams draining native vegetation catchments and 180 (169) µmol L^{-1} for streams draining catchments covered by sugarcane. The median values of CO_2 emissions were 124 (87) mmol m^{-2} d^{-1} for streams draining native vegetation catchments and 38 (49) mmol m^{-2} d^{-1} for streams draining catchments covered by sugarcane. CO_2 emissions and

Table 2. Physical, chemical, and structural characteristics of stream water draining catchments predominantly covered by either native vegetation or sugarcane plantations during different seasons. LU: land-use. ** = $p < 0.05$, *** = $p < 0.01$. Season post hoc = Dunn's test for comparisons that were significantly different among seasons. Identical season post hoc letters indicate no significant difference of water quality variables among seasons.

Water physical and chemical characteristics	Season	Native vegetation Mean	SD	Sugarcane Mean	SD	Season post hoc
Water temperature (Temp) °C	Spring	17.45	1.51	19.42	1.76	a
	Summer	20.84	0.64	22.3	0.68	b
	Winter	15.67	1.90	18.02	1.42	a
	All samples	17.99	2.61	19.64	2.27	
Comparisons temp	Season	***		LU	***	
Dissolved oxygen (DO%) Saturation %	Spring	67.40	11.65	82.61	11.89	a
	Summer	65.97	9.14	83.20	2.75	a
	Winter	80.00	7.83	90.96	7.06	b
	All samples	71.12	11.61	86.36	9.01	
Comparisons DO%	Season	***		LU	***	
Dissolved oxygen (DO) mg L^{-1}	Spring	6.49	0.97	7.46	1.11	a
	Summer	5.90	0.80	7.28	0.28	a
	Winter	7.67	0.69	8.60	0.71	b
	All samples	6.69	1.12	7.90	0.99	
Comparisons DO	Season	***		LU	***	
Electrical conductivity (Cond) μs cm^{-1}	Spring	12.43	7.02	21.96	6.09	a
	Summer	7.56	3.97	13.83	5.11	b
	Winter	14.45	6.83	18.47	6.71	a
	All samples	11.48	6.80	18.14	6.90	
Comparisons cond	Season	***		LU	***	
pH	Spring	4.98	0.79	6.15	0.38	a
	Summer	4.66	0.76	5.65	0.40	b
	Winter	5.40	0.83	6.36	0.46	a
	All samples	5.01	0.86	6.10	0.52	
Comparisons pH	Season	***		LU	***	
Oxidation–reduction potential (ORP) mV	Spring	494.91	127.22	407.25	157.80	
	Summer	558.30	111.51	398.87	99.77	
	Winter	527.71	204.59	438.49	40.61	
	All samples	526.97	156.41	418.24	105.64	
Comparisons ORP	Season	ns		LU	***	
Streamflow (Flow) L s^{-1}	Spring	12.03	5.78	9.92	4.53	a
	Summer	23.05	13.06	35.62	18.94	b
	Winter	13.03	6.51	14.88	5.47	a
	All samples	16.04	10.4	19.39	15.32	
Comparisons flow	Season	***		LU	ns	
Water velocity (Vel) m s^{-1}	Spring	0.05	0.02	0.13	0.04	
	Summer	0.05	0.02	0.18	0.05	
	Winter	0.05	0.01	0.12	0.05	
	All samples	0.05	0.02	0.14	0.05	
Comparisons vel	Season	ns		LU	***	
Dissolved inorganic carbon (DIC) mg L^{-1}	Spring	1.18	0.61	1.58	0.51	a
	Summer	0.86	0.44	1.56	0.64	ab
	Winter	0.82	0.48	1.3	0.51	b
	All samples	0.95	0.55	1.45	0.57	
Comparisons DIC	Season	**		LU	***	
Dissolved organic carbon (DOC) mg L^{-1}	Spring	1.03	0.43	0.36	0.19	
	Summer	1.47	0.91	0.45	0.39	
	Winter	1.38	0.85	0.68	0.72	
	All samples	1.29	0.79	0.53	0.55	
Comparisons DOC	Season	ns		LU	***	
Total dissolved carbon (TDC) mg L^{-1}	Spring	2.23	0.79	1.94	0.58	
	Summer	2.32	1.07	2.01	0.88	
	Winter	2.20	1.08	1.98	0.86	
	All samples	2.25	0.99	1.98	0.80	
Comparisons TDC	Season	ns		LU	ns	
Total dissolved nitrogen (TDN) mg L^{-1}	Spring	0.09	0.15	0.4	0.17	
	Summer	0.15	0.18	0.44	0.28	
	Winter	0.15	0.19	0.33	0.22	
	All samples	0.13	0.18	0.38	0.23	
Comparisons TDN	Season	ns		LU	***	

concentrations were significantly different among seasons ($p < 0.01$; Fig. 2c–d). The CO_2 concentrations were higher during the summer and did not differ between spring and winter. The CO_2 fluxes were higher during summer.

Variables affecting CO_2 concentrations in tropical streams

The most important variable affecting CO_2 concentrations in tropical streams was stream water pH (Fig. 3);

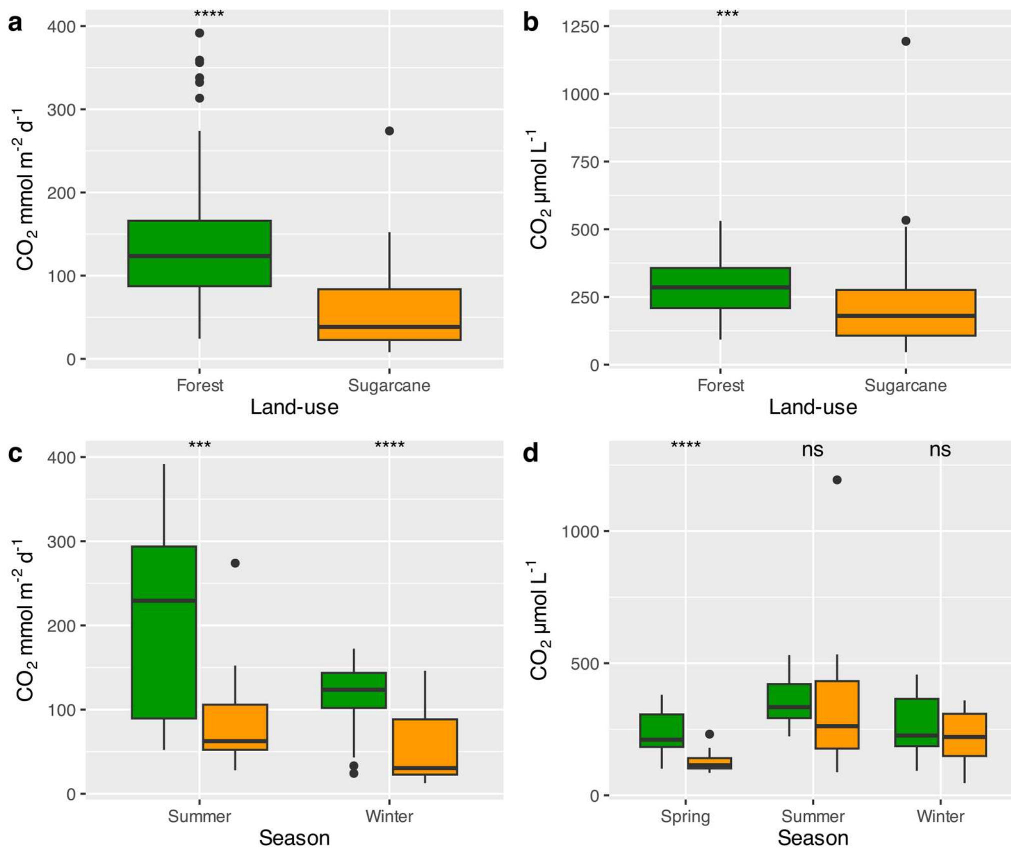

Figure 2. CO_2 emissions and concentrations in the studied streams across different land uses and seasons. (a) CO_2 fluxes across land-uses; (b) CO_2 concentrations across land-uses; (e) CO_2 fluxes across seasons; and (f) CO_2 concentrations across seasons. **** = $p < 0.001$; *** = $p < 0.01$; ns = not significantly different. Green box plots represent streams draining native vegetation catchments and orange box plots represent streams draining sugarcane fields.

other important variables included water conductivity, season, CH_4 concentration, and total dissolved nitrogen (Fig. 3). Partial dependence plots revealed a negative relationship between CO_2 and pH and between water conductivity and CO_2 concentrations during summer and a positive relation between CO_2 and CH_4 (Fig. 4).

Discussion

Our first hypothesis was that streams draining sugarcane fields would show greater CO_2 emission and concentration because of the carbon input from sugarcane crops and fertilizer application. Our results did not support this hypothesis; streams draining native vegetation catchments showed higher CO_2 emissions and concentrations. The main explanation for these results is the elevated soil respiration in native vegetation catchments that delivers CO_2 through groundwater paths. Soil respiration is highly dependent on soil carbon, moisture, and porosity, found especially in the riparian and catchment areas of headwater streams because of the close connection of the stream channel with the adjacent land (Freeman et al. 2007). In these areas, aeration induced by the riparian vegetation roots (Goodrick et al. 2016) and constant deposition of above- and below-ground organic matter is elevated, especially in the tropics (Cusack et al. 2018). The amount of organic matter input in soils from sugarcane cultivation is lower than that from native vegetation (e.g., Cerrado vegetation), despite the input from sugarcane residues. In addition, the use of heavy machinery causes soil aggregate breakdown, which reduces the carbon content (Coonan et al. 2020), and therefore less organic matter is transferred and transformed in the soil and delivered into headwater streams. A study comparing the soil carbon content in forests and sugarcane fields revealed that the soil carbon content can be ~60% lower in sugarcane fields than in native vegetation areas (Franco et al. 2015). For our streams, the median CO_2 concentrations were ~60% lower in streams draining sugarcane fields than in native catchments. When comparing soil respiration between sugarcane fields and savannas in studies conducted near the study site, CO_2 fluxes in sugarcane fields averaged ~2 µmol $CO_2\ m^{-2}\ s^{-1}$ (Luiza et al. 2015), whereas soil respiration in savannas were much higher, averaging 8 mol $CO_2\ m^{-2}\ s^{-1}$ (Da Rocha et al.

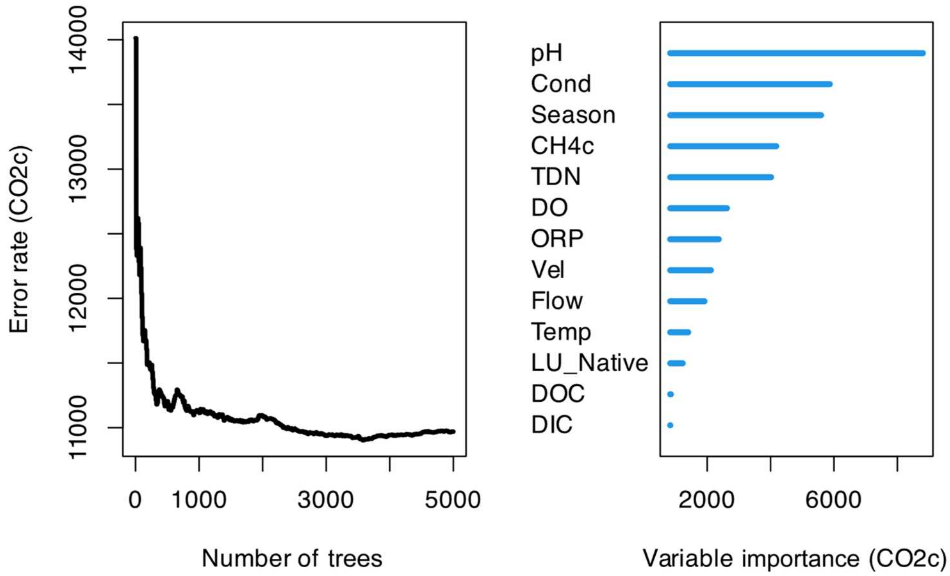

Figure 3. Results from the random forest model showing the stabilization of the error rate across the number of trees in the model (left) and the ranking of the variable importance (right, $R^2 = 0.45$) for explaining CO_2 concentrations (CO2c) in the studied streams. Cond = water conductivity; CH4c = methane concentration; TN = total dissolved nitrogen concentrations; DO = dissolved oxygen concentrations; ORP = oxidation reduction potential; Vel = water velocity; Flow = streamflow; Temp = water temperature; DIC = dissolved inorganic carbon concentrations; DOC = dissolved organic carbon concentrations; LU_Native = percentage of native vegetation in the catchment.

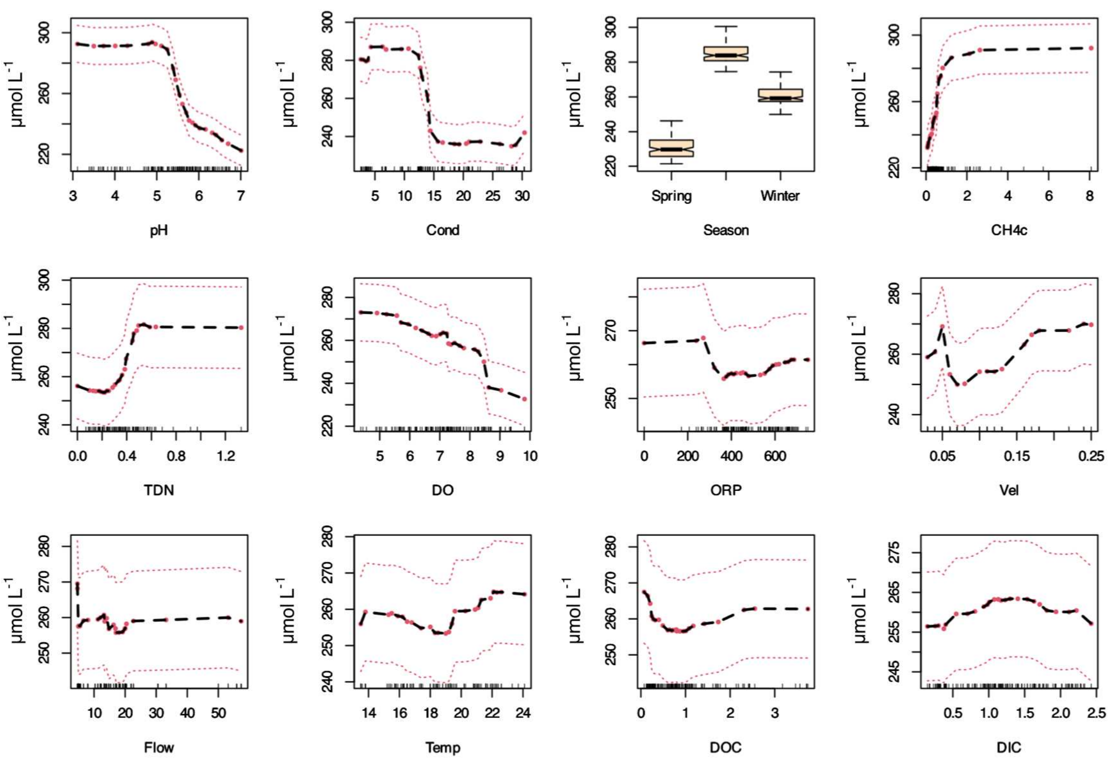

Figure 4. Partial dependence plots showing the relationships between CO_2 concentrations and the physical and chemical variables considered in the model. CO_2 concentrations (vertical axis) and the physical and chemical variables considered in the model (horizontal axis). Cond = water conductivity (mS cm^{-1}); CH4c = methane concentration (mmol L^{-1}); TDN = total dissolved nitrogen concentration (mg L^{-1}); DO = dissolved oxygen concentration (mg L^{-1}); ORP = oxidation reduction potential (mV); Vel = water velocity (m s^{-1}); Flow = streamflow (L s^{-1}); Temp = water temperature (°C); DIC = dissolved inorganic carbon concentration (mg L^{-1}); DOC = dissolved organic carbon concentration (mg L^{-1}). Season = boxplots representing the CO_2 concentrations in the spring, summer, and winter seasons. Red lines represent the 95% confidence intervals of the model.

2002). The effects of liming can also be important for CO_2 dynamics because it is used in sugarcane cultivation to correct soil acidity (Cherubin et al. 2015) and can shift CO_2 emissions. Therefore, our results demonstrate that sugarcane-dominated catchments may contribute less CO_2 to their receiving headwaters than native vegetation catchments, as also found in subtropical streams (Andrews et al. 2021).

The second hypothesis of this study was that CO_2 emissions would be greater during the summer because of increased temperature and streamflow, which would alter the gas transfer velocity. Our results corroborate this hypothesis because CO_2 emissions were greater during the summer in both land uses. These results can be explained by the higher soil and water temperatures during the summer, which accelerates the root and microbial metabolic leading to a high decomposition rate in tropical soils and streams (Brown et al. 2004, Saltarelli et al. 2018, Marzolf and Ardón 2021, Peralta-Maraver et al. 2021). In addition, tropical summer is characterized by a wet season with constant rains and storms, increasing soil respiration, streamflow, water turbulence, gas transfer velocity, and terrestrial organic carbon delivery into stream channels because of high microbial activity, organic matter accumulation, root metabolism, and nutrient cycling (Tonin et al. 2017). Flushing events can also deliver terrestrially derived carbon dioxide that accumulates in the soil and groundwater into streams (Bodmer et al. 2016). Together, these factors contribute to higher CO_2 emissions during the tropical summer, especially in native vegetation catchments.

The third hypothesis of this study was that the most important variables controlling CO_2 concentrations would be related to DOC and total dissolved nitrogen in streams. Our results did not support this hypothesis because the most important variables explaining CO_2 concentrations were pH, conductivity, season, and CH_4 concentration. Total dissolved nitrogen was the fifth ranked variable in the random forest variable importance analysis, and DOC concentration was among the last variables regarding importance in explaining the results. The relationship between CO_2 and pH can be explained by the controlling capacity of pH on soil microbial respiration (Sitaula et al. 1995, Chen et al. 2016). In addition, soil pH can affect water conductivity, considering that the soil acidification and texture can also change the cationic characteristics in belowground processes, especially in soils with poor capacity in retaining cations and ions (Meng et al. 2019). Therefore, we believe that the relation between pH and water conductivity with CO_2 concentrations is indicative of groundwater inputs. Tropical headwater streams draining small catchments are dependent on groundwater inputs, which are rich in dissolved gases because of soil respiration, representing ~77% of the carbon transported from the landscape by streams (Johnson et al. 2008).

Another interesting result was the relationship between CO_2 and CH_4 concentrations in our study. A recent study showed that approximately half of the dissolved CH_4 pool in streams is oxidized before emission (Robison et al. 2022), indicating that this process may be relevant for our studied streams, as shown by the random forest model. In addition to not being an important factor for CO_2 concentrations in the streams, the concentration of DOC and DIC was much lower than the global averages, but the studies that calculated the global averages do not include data from Brazil and the studied region (Liu and Wang 2022, Cole and Prairie 2024). In another study conducted in regions close to this study, the concentrations of DOC and DIC were similar to those found in this study (Taniwaki et al. 2017a).

This study was limited in understanding the nictemeral variations in CO_2 emissions and the effects of rains and streamflow rises on CO_2 concentrations and emissions. A study in temperate streams showed that CO_2 emissions in streams are different during day and night periods (Schelker et al. 2016). We are aware of this finding and believe those studies would greatly enrich the understanding the carbon cycle dynamics in tropical catchments and headwaters, despite the difficulties in terms of funds and security to conduct these studies.

Future studies analyzing the impacts of sugarcane cultivation on carbon dynamics should evaluate several gaps in the understanding of tropical stream carbon cycles. For example, the effects of soil pH correction through soil liming on CO_2 emissions in tropical streams is unknown. Liming, a common practice in sugarcane cultivation (Cherubin et al. 2015), is applied at ~3 t ha^{-1} every 2 years and can have direct impacts on carbonate systems in freshwater ecosystems, thus impacting CO_2 dynamics (Oh and Raymond 2006, Raymond et al. 2008, Lauerwald et al. 2013). The effects of soil texture can also be an important factor in determining CO_2 emissions, considering that different soils have different capacities in retaining organic matter delivered into the stream channels. Another missing piece is the quantification of the contributions of CH_4 oxidation to CO_2 emissions in tropical streams, considering that tropical catchments are subjected to greater carbon inputs from tropical forests and higher temperatures. Because Brazil produces ~39% of the global sugarcane in the world, understanding these gaps would provide better comprehension of the effects of sugarcane production on freshwater carbon cycles in (Zheng et al. 2022).

Conclusion

Our study showed that CO_2 emissions and concentrations are higher in streams draining native vegetation catchments because of the greater soil respiration and carbon stocks in the soil, resulting in higher CO_2 concentrations in groundwater subsequently delivered to headwater streams. CO_2 emissions and concentrations are higher during summer, primarily affected by higher temperatures and rainfall, which are known to increase metabolic rates and microbial activities in soil and streams. Therefore, this study demonstrates the interplay between terrestrial and aquatic ecosystems in the CO_2 dynamics in catchments and headwater streams.

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Data availability

The data used for this study are available in Taniwaki, R.H. 2024. CO_2 concentrations and emissions from subtropical headwater streams, São Carlos, Brazil, 2018 ver 1. Environmental Data Initiative. https://doi.org/10.6073/pasta/9ce8e2bc0fc472544c621e4658bdc6a4.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Author information

RHT designed the study, wrote the manuscript, conducted field sampling and conducted the statistical analysis. EHS, JBC, and DGFC helped design and discuss the results. CBB, MSF, and M VFhelped with field sampling and sample analysis. LAM was responsible for funding acquisition and reviewing the manuscript. LCS and SP substantially reviewed the manuscript.

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