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Greenhouse gas dynamics in tropical montane streams of Puerto Rico and the role of watershed lithology

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Abstract The major greenhouse gases in streams and rivers, carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), can contribute significantly to regional greenhouse gas (GHG) budgets, and each appears to be responding to multiple drivers. Recent work suggests that tropical water bodies may be hot spots of GHG emissions due to high primary productivity in their watersheds, but tropical streams and rivers have historically been underrepresented in studies of GHG concentration and emissions. We use a five-year record of weekly water chemistry and dissolved gas data from eight tropical watersheds of varying lithology and redox conditions in the Luquillo Mountains of Puerto Rico to examine controls on GHG variability and estimate gas flux. Streams were frequently supersaturated in all three gases indicating that streams in this tropical landscape are sources of GHGs to the atmosphere. Concentrations of CO_2 and N_2O were associated with lateral inputs from the surrounding landscape, whereas CH_4 concentrations correlated with in-stream oxygen availability and lithology. Our results underscore the importance of including tropical sites in global syntheses and budgets and the role of both in-stream biological and physical processes as well as landscape attributes that contribute to the export of gases to the fluvial network and atmosphere.

Keywords Greenhouse gas · Carbon dioxide · Methane · Nitrous oxide · Tropical · Stream

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Introduction

Streams and rivers are important sources of carbon dioxide (CO_2; Cole et al. 2007; Drake et al. 2018), methane (CH_4; Stanley et al. 2016), and nitrous oxide (N_2O; Quick et al. 2019) to the atmosphere. Our current understanding of greenhouse gas (GHG) patterns, controls, and fluxes is driven primarily by studies coming from temperate and populated areas (e.g., Stanley et al. 2016), with an underrepresentation of Arctic and tropical zone latitudes (Lauerwald et al. 2015). Although there is a comparatively small number of studies on CO_2 outgassing from tropical systems, a recent synthesis suggests a disproportionate contribution of CO_2 from subtropical and equatorial

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regions to global riverine fluxes (Lauerwald et al. 2015). It has yet to be determined if fluvial emissions of CH_4 and N_2O from tropical regions are similarly important to global estimates. Our ability to accurately quantify GHG fluxes from tropical ecosystems is limited by a paucity of studies and uneven and spatiotemporally limited data coverage. Although a recent global synthesis included tropical CH_4 emissions from 23 different studies, all were classified as 'rivers', suggesting that there is a gap in studies measuring GHGs in smaller streams in the tropics (Rosentreter et al. 2021). There is a need for direct, long-term measurements of GHGs from diverse tropical ecosystems to more accurately represent the role of tropical inland waters in global GHG fluxes.

Given the aseasonality, warm temperatures, hydrological extremes, and unique disturbance regimes that characterize much of the tropics, it is reasonable to expect varying patterns and controls on GHG concentrations compared with other biomes. The knowledge that we do have about controls on GHG concentrations and fluxes in tropical systems is dominated by studies from the Amazon basin that have primarily focused on CO_2 dynamics (Lauerwald et al. 2015). Inflow of dissolved carbon and CO_2 from groundwater, soil respiration, and wetlands have been identified as primary drivers of CO_2 in many tropical and subtropical regions (Sadat-Noori et al. 2016; Duvert et al. 2019; Abril and Borges 2019; Schneider et al. 2020), corroborating the importance of landscape contributions to stream CO_2 dynamics as also reported from temperate systems (Hotchkiss et al. 2015; Herreid et al. 2020). There is a growing number of studies measuring CH_4 in tropical systems (e.g., Selvam et al. 2014; Teodoru et al. 2015; Bange et al. 2019; Rosentreter al. 2021), however, considerably less emphasis has been placed on patterns of CH_4 and N_2O concentrations in the tropics, particularly when considering factors driving the production of CH_4 and N_2O (though see Borges et al. 2015; Upstill-Goddard et al. 2017). Spatial variability in CH_4 and N_2O may be considerable in some tropical locations, especially those characterized by strong redox gradients (Liptzin et al. 2011; Liptzin and Silver 2015).

Few studies investigate controls and mechanisms driving variability in concentrations and fluxes of all three major GHGs (CO_2, CH_4, N_2O) when measured together, which is essential for improving global models and developing a better understanding of factors driving GHG dynamics across biomes. Here, we use a five-year record of weekly data from eight streams and rivers within the Luquillo Mountains in Puerto Rico to examine potential controlling mechanisms and provide flux estimates of CO_2, CH_4, and N_2O in tropical montane watersheds with differing lithologies and forest types (McDowell et al. 2021). We hypothesize that the availability of dissolved organic carbon (DOC) will drive collective gas concentrations, given the need for an energy source for many gas-producing pathways. We hypothesize that CO_2 will be tightly linked to in-stream dissolved oxygen (O_2) concentrations due to the links between respiration and primary production. However, we expect this relationship to diverge from the theoretical 1:1 ratio given potential CO_2 inputs from anaerobic respiration and external inputs from the surrounding landscape (Crawford et al. 2014). We expect CH_4 to be related to conditions favorable for methanogenesis (i.e., low O_2, high DOC, small sediment size; Stanley et al. 2016), and N_2O to be related to the availability of dissolved nitrogen (nitrate, ammonium, total dissolved nitrogen) and O_2 given the requirements of N_2O-producing pathways (Quick et al. 2019).

Methods

Site description

Study sites are located in the Luquillo Experimental Forest of northeastern Puerto Rico (Fig. 1; McDowell et al. 2021). Compared with flat, lowland tropical sites, our study region includes watersheds that drain mountainous, steep gradient tropical landscapes. The average air temperature in the Luquillo Mountains is above 20 °C with rainfall varying from 2500 to 4500 mm depending on elevation (McDowell et al. 2012; Murphy et al. 2017). The Luquillo Mountains vary in lithology, and streams and rivers that drain the mountain landscape reflect these differences in lithology (Wymore et al. 2017; Hynek et al. 2022). Our study sites (Table 1) are paired and include a larger mainstem river and a smaller tributary stream in each of the three dominant lithologies (volcaniclastic, quartz diorite, and hornfels). Differences in lithology result in different weathering regimes, variable oxygen availability and contrasting stream channel attributes, with sand-filled channels typical in

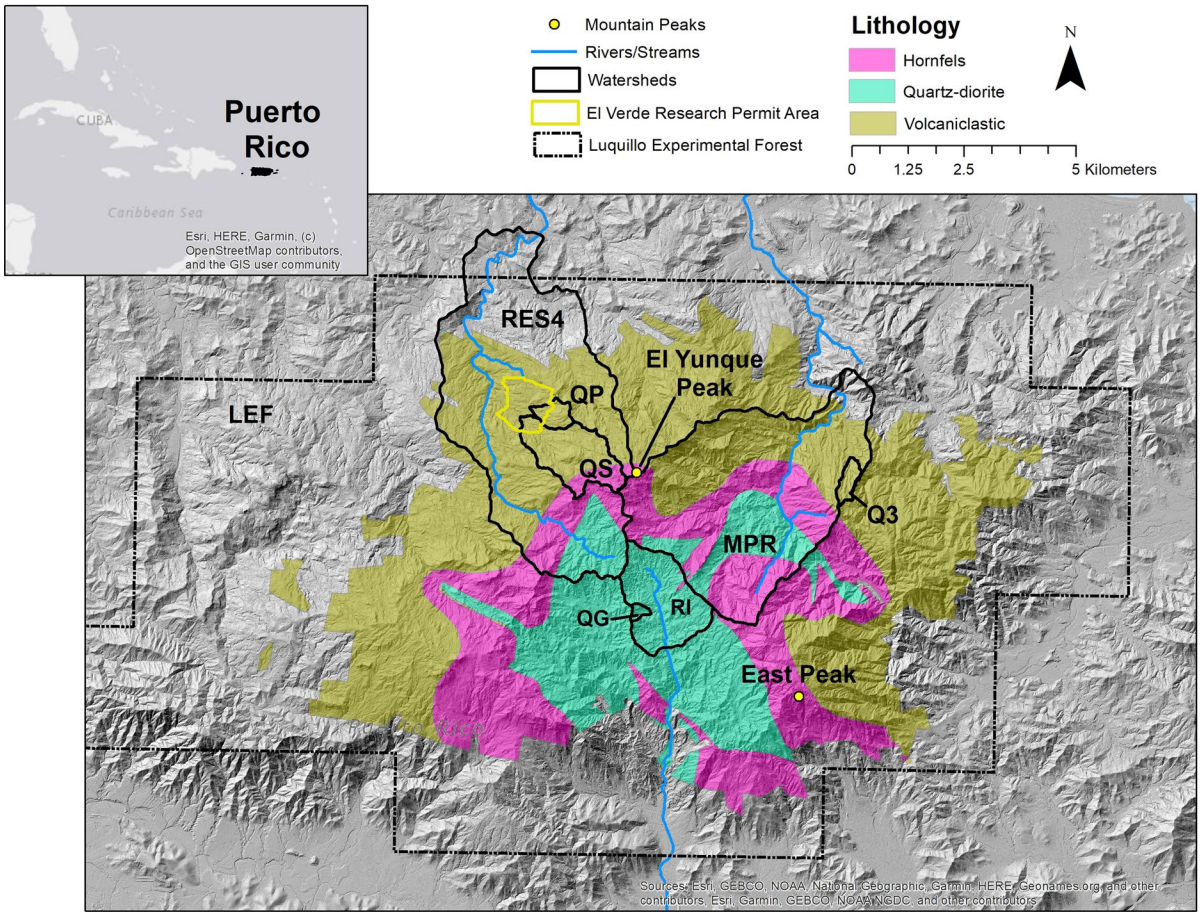

Fig. 1 Map of the Luquillo Mountains and the Luquillo Experimental Forest in Puerto Rico. Watersheds are outlined in black, and colors denote major lithology types. RI: Río Icacos; QG: Quebrada Guabá; MPR: Mameyes at Puente Roto; Q3: Bisley 3; RES4: Río Espíritu Santo; QS: Quebrada Sonadora; QP: Quebrada Prieta. QPA and QPB are located near the point labeled QP, with the two tributaries (QPA, QPB) sampled before the confluence. Map provided by Miguel Leon and used with permission

high-elevation watersheds underlain by quartz diorite, and large boulders in steeply sloped streams draining volcaniclastic and hornfels landscapes (Pike et al. 2010; McDowell et al. 2021).

Data collection

Our dataset includes weekly water chemistry and dissolved gas data collected between April 2015 and December 2019, resulting in a total of 965 observations across the eight sites. One water and one gas sample were collected at each stream during each sampling event. Water chemistry samples were collected in acid-washed syringes and filtered using pre-combusted glass fiber filters (0.7 µm; Whatman GF/F) and stored on ice immediately following collection. Samples were frozen or refrigerated until the time of analysis. Dissolved oxygen, specific conductance, pH, and water temperature measurements were recorded at the time of sample collection using a YSI multiparameter probe (YSI ProDSS, Yellow Springs, OH). Dissolved gas samples were collected using acid-washed syringes equipped with three-way stopcocks. Syringes were rinsed and filled to 30 mL underwater after clearing air bubbles. Syringes were kept on ice and were equilibrated into a headspace of ultrapure helium and stored in evacuated vials within eight hours of collection.

Substrate particle size was characterized at three of the streams (QP, QS, and RI) based on the smallest

Table 1 Characteristics of study watersheds: watershed area (Area km^2); mean catchment slope (Slope, °); mean elevation at sampling location (Elevation, Meters Above Sea Level); Lithology: Volcaniclastic (% VC); Quaternary (% Q); Quartz Diorite (% QD); and Hornsfel (% Hf); and Vegetation: Sierra Palm (% SP); Colorado (% Co); Dwarf Palm (% DP); and Tabonuco (% Tab)

Watershed	Area (km^2)	Slope (°)	Elevation (MASL)	Lithology				Vegetation			
				% VC	% Q	% QD	% Hf	% SP	% Co	% DP	% Tab
MPR	17.7	22.6	498	38.8	0.1	20.3	40.8	19	13	5	60
Q3	0.28	20.9	543	100.0	0.0	0.0	0.0	0	0	0	100
RI	3.3	14.6	686	0.0	0.0	99.4	0.6	20	78	2	0
QG	0.13	17.5	643	0.0	0.0	100.0	0.0	0	100	0	0
QS	2.6	17.4	740	66.1	0.0	0.0	33.9	32	53	7	8
QP	0.31	15.9	431	100.0	0.0	0.0	0.0	66	0	0	34
QPA	0.03	18.5	507	100.0	0.0	0.0	0.0	100	0	0	0
QPB	0.16	16.3	582	100.0	0.0	0.0	0.0	93	7	0	0

Organized where downstream river is bold faced and nested tributaries are indented

size opening that the substrate could pass through on a gravelometer. Ten transects were established roughly 10 m apart along a ~ 100 m reach. At each transect, ten substrate readings were taken along the width of the stream. Median (d50) substrate size was determined from cumulative frequency distributions.

Water chemistry analysis

Surface water samples were analyzed for concentrations of ammonium (NH_4^+), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), silica (SiO_2 (aq)), and major cations (magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), and sodium (Na^+)) and anions (chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-})). Major cations and anions were measured using ion chromatography (Anions/Cations Dionex ICS-1000/1100). NH_4^+, SiO_2 (aq), and phosphate as SRP were analyzed using a Seal Analytical AQ2 or SmartChem 200 discrete automated colorimetric analyzer. Measures of NH_4^+ and NO_3^- refer to N only and are reported as NH_4-N and NO_3-N. DOC and TDN were measured by high-temperature catalytic oxidation with a Shimadzu TOC-L with a TNM-1 nitrogen analyzer.

Dissolved gas analysis

Each syringe was filled with 30 mL of helium and samples were shaken for 5 min to equilibrate gases between water and headspace (Mulholland et al. 2004). The headspace was then stored in 20 mL evacuated vials for subsequent analysis at the University of New Hampshire. Gas samples were analyzed using a Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity detector to detect CO_2, a flame ionization detector for CH_4, and an electron capture detector to detect N_2O. Gas concentrations are reported in µM and the percentage saturation of each gas concentration was determined following standard procedures (Audet et al. 2017; Herreid et al. 2020).

Gas flux calculations

Gas flux estimations for each gas at a subset of study streams (QP, QS, and RI) were estimated using the following equation:

$$F = k(C_w - C_{eq})$$

where k (gas transfer velocity) is multiplied by the difference between the dissolved gas concentration in the water (C_w) and the gas concentration expected at equilibrium with the atmosphere (C_{eq}) (Beaulieu et al. 2011; Raymond et al. 2012). Gas transfer velocities were estimated using two approaches. Field measurements of reaeration coefficients were conducted at each site and used to calculate k. Reaeration coefficients were determined in the field using argon (Ar) as a conservative gas tracer. Background samples were collected at several stations along the reach prior to

conducting an addition of Ar. Ar was co-injected into the stream with NaCl at a constant rate. Conductivity was measured at the furthest downstream station. After detecting that conductivity had reached plateau, we recorded measurements of specific conductance, stream temperature, and barometric pressure, and collected water samples for Ar:N_2 (triplicate) and water chemistry at stations along the stream reach. The NaCl data were used to calculate travel time and discharge. Stream width and mean depth were measured at each station and were used with discharge to calculate velocity. Reaeration coefficients were then calculated following standard methods (Supplementary Table 1; Wanninkhof et al. 1990; Raymond et al. 2012). Slope and velocity of each stream reach were also used to model *k* using Eq. 3 from Raymond et al. (2012). We considered using the framework from Ulseth et al. (2019) for determining *k*, but ultimately determined that not all of our streams fall into the steep, high-energy category that would be considered well-suited for this approach. Instantaneous discharge measurements used in flux calculations were obtained from gauging stations of the United States Geological Survey (QS: 50063440; RI: 5007500) and the University of Puerto Rico (QP). We did not collect ebullitive CH_4 samples and thus our flux estimates represent diffusive CH_4 flux only.

Statistical analyses

Data were normalized using logarithmic transformations if they failed Shapiro–Wilk tests for assumptions of normality or exhibited high levels of skewness and kurtosis. Boxplots in combination with analysis of variance (ANOVA) and means separation were used to identify differences among sites and lithologies for each gas. We assessed bivariate relationships between dissolved gas concentrations and metrics of stream chemistry and environmental parameters using linear regression analysis. We present the relationship between dissolved CO_2 and O_2 as excess CO_2 and O_2. Excess was calculated as the difference between measured CO_2 or O_2 concentrations and equilibrium concentrations expected if the stream water was in equilibrium with the atmosphere (i.e., 100% saturation). Thus, positive values indicate periods of supersaturation and negative values indicate depletion or undersaturation. If aerobic metabolism accounts for the majority of measured CO_2 concentrations, data should largely fall on a 1:1 line (with a − 1 slope), but anaerobic respiration and large terrestrial inputs of CO_2 often cause this relationship to change (Crawford et al. 2014; Herreid et al. 2020). All statistical analyses were performed using R version 4.0.5 (R Core Team 2021) with an $\alpha < 0.05$ being the significance threshold for all analyses.

Results

Water chemistry and dissolved gases

Average concentrations of NO_3^- ranged from 0.09 to 0.29 mg N L^{-1} across sites and mean DOC concentrations were between 1.01 and 1.88 mg C L^{-1} (Supplementary Table 2). Mean concentrations of other measured water chemistry analytes by site can be found in the supplemental material. Dissolved CO_2 concentrations ranged from 3.4 to 487 µM (mean = 90 µM) across all sites over the length of the dataset. Streams were almost always supersaturated in CO_2 (mean = 791% saturation) and exhibited minimal spatial variability among sites and between mainstem-tributary pairings (Fig. 2a; Table 1). Dissolved CH_4 concentrations ranged from 3.5×10^{-3} to 3.0 µM (mean = 0.22 µM) and varied among sites (Fig. 2b). The two watersheds primarily underlain by quartz diorite, RI and QG, had significantly higher CH_4 (% saturation) than all other sites ($p < 0.0001$), with QG being significantly lower than RI ($p < 0.0001$). All sites showed consistent supersaturation in CH_4 (mean = 9.164% saturation). Streams were generally supersaturated in N_2O (mean = 181% saturation) and did not vary greatly among sites (Fig. 2c). Concentrations of dissolved N_2O ranged from 1.1 to 46 nM (mean = 13 nM) across sites.

Substrate particle size

Median particle size varied among sites and lithologies (Supplementary Table 3). Substrate at RI, underlain by quartz diorite, is predominantly sand (77%) with a d50 of 1.65 mm. QP had a d50 of 18.70 mm, and median particle size at QS was 160 mm.

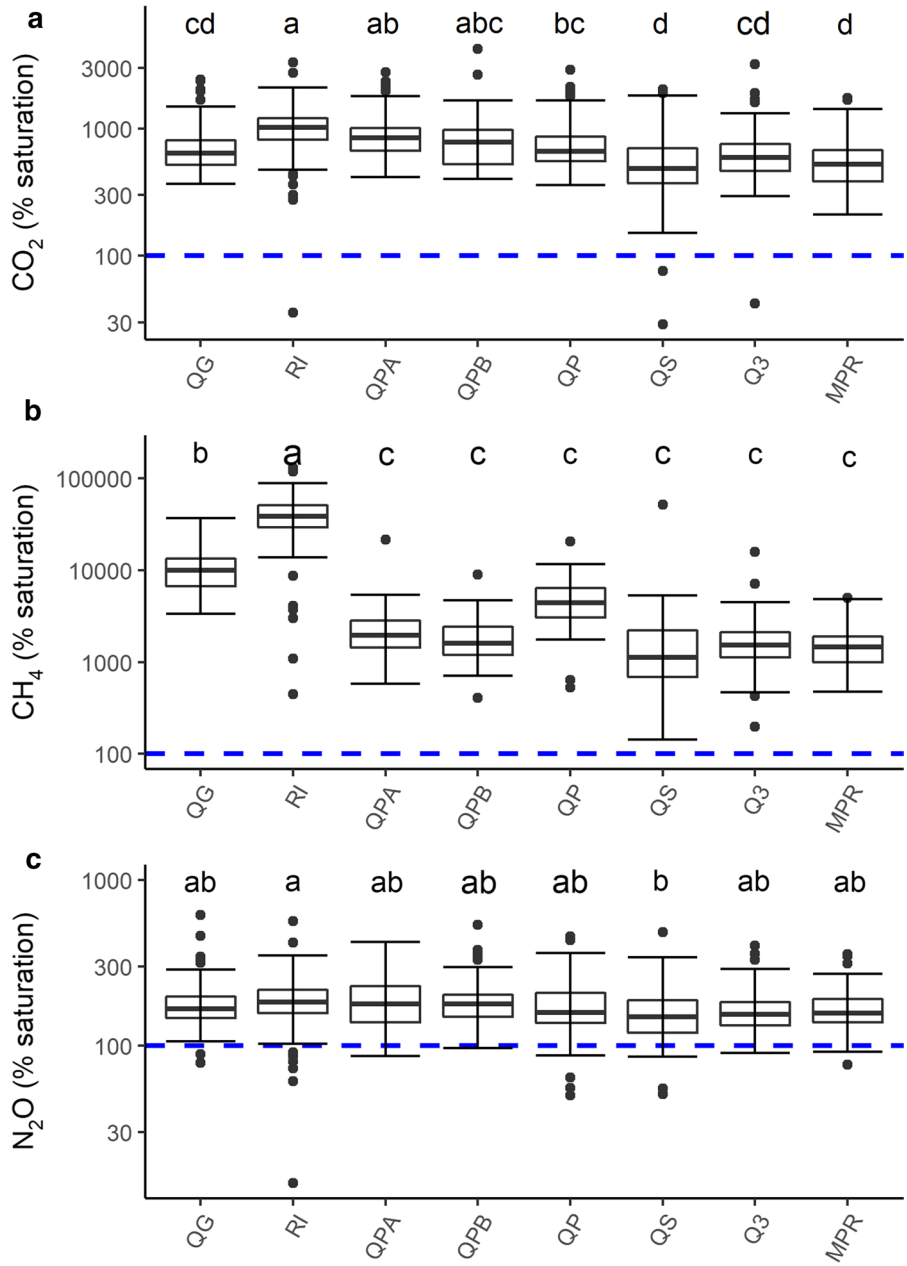

Fig. 2 Boxplot panels representing percent saturation for CO_2 (**a**), CH_4 (**b**), and N_2O (**c**) across the sampling period at 8 sites (n = 747). Sites are organized by nested watershed (see Table 1). Letters indicate statistically significant differences for between site comparisons. Data that fall above the dashed blue line at 100% indicate periods of supersaturation. Note that the y-axis of each panel is presented in log scale

Fluxes of GHGs

Fluxes calculated from modeled *k* were higher than those using measured *k* for RI and QP and lower for QS (Table 2). How and whether fluxes varied significantly among sites was dependent on if fluxes were calculated from modeled or measured *k* (see significance groupings in Table 2). Across the three streams, mean CO_2 flux calculated from measured *k* was 1.84 mol m^{-2} d^{-1}, mean diffusive CH_4 flux was 1.79 mmol m^{-2} d^{-1}, and mean N_2O flux was 194 µmol m^{-2} d^{-1}. On average, fluxes using modeled *k* were higher: mean CO_2 flux was 4.27 mol m^{-2} d^{-1}, mean diffusive CH_4 flux was 30.03 mmol m^{-2} d^{-1}, and mean N_2O flux across sites was 307 µmol m^{-2} d^{-1}.

Table 2 Mean gas transfer velocity (k, m d^{-1}), and fluxes of CO_2 (mol m^{-2} d^{-1}), CH_4 (mmol m^{-2} d^{-1}), and N_2O (µmol m^{-2} d^{-1}) calculated using measured and modeled values for gas transfer velocity for each site.

	QS		QP		RI		Mean flux	
	Measured	Modeled*	Measured	Modeled*	Measured	Modeled*	Measured	Modeled*
k	87.4 (104.8)	22.0 (12.3)	6.5 (10.6)	14.4 (18.3)	2.8 (5.0)	78.5 (39.5)	–	–
CO_2 flux	4.76 (6.16)^a	1.25 (0.96)^b	0.56 (1.11)^b	1.25 (1.97)^b	0.16 (0.27)^b	9.43 (6.01)^a	1.84 (4.20)	4.27 (5.51)
CH_4 flux	3.22 (4.71)^a	0.94 (1.87)^b	0.67 (1.01)^b	1.59 (1.76)^b	1.35 (1.87)^b	79.1 (50.2)^a	1.79 (3.20)	30.03 (48.44)
N_2O flux	509 (1,272)^a	118 (190)^b	59.0 (248.6)^b	122.6 (437.0)^b	10.7 (25.5)^b	627 (707)^a	194.3 (785.2)	307.4 (557.7)

Standard deviation in parentheses

*Modeled using Eq. 3 fromRaymond et al. (2012)

Superscripts indicate significant differences between streams ($p < 0.05$)

Drivers of GHGs

We found that lithology plays a strong role in regulating the relative magnitude of gases, particularly for CH_4. Methane (as % saturation) was significantly higher and more variable in the quartz diorite sites than in the volcaniclastic or mixed lithologies (Fig. 3). Carbon dioxide varied significantly among lithologies with quartz diorite sites being the highest, and volcaniclastic sites higher than mixed sites (Fig. 3). Nitrous oxide was more uniform across lithologies, with quartz diorite sites only being significantly higher than the sites with mixed lithologies (Fig. 3). We found no relationships between DOC and any of the three gases.

Contrary to our hypothesis, the negative relationship between excess CO_2 and excess O_2 was weak ($r^2 = 0.07$, $p < 0.0001$, Fig. 4). Carbon dioxide was generally supersaturated while O_2 was generally depleted, except at MPR (mixed lithology) where O_2 was frequently above 100% saturation. The majority of data points fall to the right of the theoretical 1:1 line and excess CO_2 spanned a much larger range (− 10 to 475 mmol m^{-3}) than O_2 (− 60.2 to 16.5 mmol m^{-3}).

Simple linear regression analysis revealed a significant negative relationship between dissolved CH_4 and oxygen concentrations ($r^2 = 0.48$, $p < 0.0001$, Fig. 5). Methane concentrations did not correlate with any cations or anions. Similarly, and in contrast to our hypothesis, we found no relationships between N_2O and NO_3^-, NH_4^+, TDN, dissolved O_2 or any other measured water chemistry analyte.

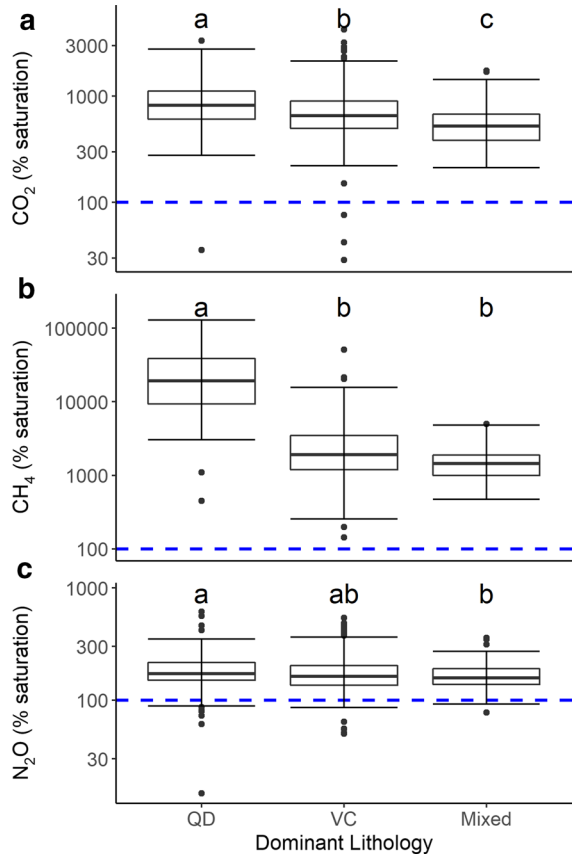

Fig. 3 Boxplot representing differences between CO_2 (**a**), CH_4 (**b**) and N_2O (**c**) across the dominant lithology types (QD = Quartz Diorite, VC = Volcaniclastic). Letters indicate statistically significant differences (n = 747)

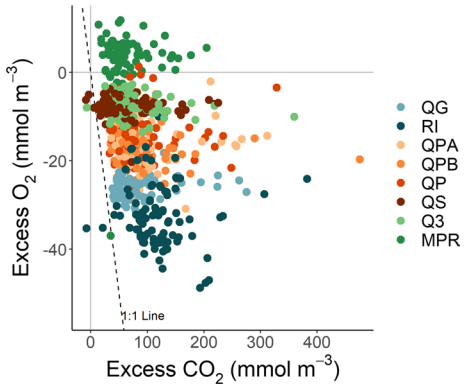

Fig. 4 Relationship between excess CO_2 and O_2 (n = 662). Excess was calculated as the difference between measured and expected equilibrium concentrations (100% saturation). The dashed 1:1 line represents the theoretical relationship under the assumption that aerobic metabolism accounts for the majority of measured CO_2 concentrations

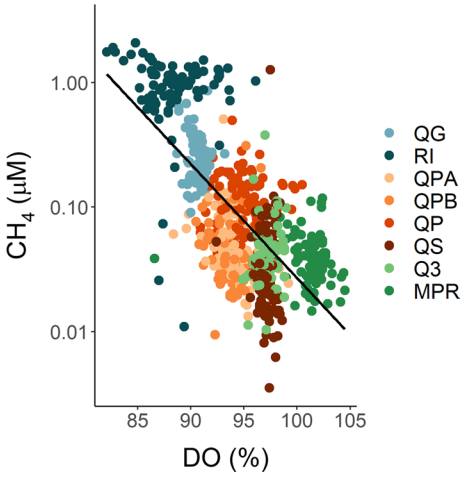

Fig. 5 Linear regression between dissolved CH_4 and oxygen across all sites ($r^2 = 0.48$, $p < 0.0001$, n = 685). Note that the y-axis is presented on a log scale

Discussion

Lithology and landscape contributions appear to drive GHG dynamics in watersheds within the Luquillo Mountains. Methane concentrations are largely a result of in-stream production, inferred from the negative relationship with dissolved O_2 as well as the differences between sediment size (Pike et al. 2010, Supplementary Table 3) and redox status (Liptzin and Silver 2015) among lithologies. Concentrations of CO_2 and N_2O, in contrast, showed little variation with stream chemistry or other characteristics of our study streams, suggesting that lateral inputs from the terrestrial landscape may contribute to the variability in stream CO_2 and N_2O concentrations. Production of CO_2 through anaerobic respiration pathways may also contribute to CO_2 variability and deviation from the theoretical 1:1 relationship with dissolved O_2 (Fig. 4). Variability in mechanisms driving GHG dynamics, in our study and others, suggests different controls and patterns of GHGs in fluvial ecosystems globally. Our flux estimates, along with saturation calculations, suggest that streams and rivers in the Luquillo Mountains are generally sources of CO_2, CH_4, and N_2O to the atmosphere. For all but one pair (CO_2 and CH_4 in QG and RI) in our nested watershed sampling design, the smaller tributary stream was just as supersaturated in all three gases as the larger mainstem river. This suggests that headwater and low-order streams may be disproportionate contributors of GHGs relative to larger rivers. The magnitude of the fluxes from this study in comparison with previous studies indicates that tropical inland waters may be important on the global scale for all three gases, not only CO_2 (Lauerwald et al. 2015).

Drivers of greenhouse gases

Stream water CO_2 and N_2O concentrations in the Luquillo Mountains are likely a result of lateral inputs from the terrestrial landscape. Contrary to our hypothesis, we did not observe relationships between any of the greenhouse gases and DOC concentrations. It is possible that although the availability of DOC is important for gas production, we were not able to detect relationships in these low-DOC streams where consumption of labile DOC is rapid (Rodríguez-Cardona et al. 2021). We found no relationship between N_2O and NO_3^-, TDN, or NH_4^+ even though N_2O concentrations are generally tightly linked to dissolved N and O_2 availability (Burgin and Hamilton 2007; Quick et al. 2019) and relationships between N_2O and NO_3^- have been observed in riparian groundwater at one of our sites (RI; McDowell et al. 1992). However, our finding that N_2O is unrelated to concentrations of dissolved N is consistent with other tropical rivers (Borges et al. 2015; Bange et al. 2019) and suggests that production of N_2O is occurring in riparian zones due to the strong redox gradients and

Table 3 Comparisons of ranges of excess CO_2 and O_2 from other studies. Means reported if available

Study	Biome	O_2 excess range	CO_2 excess range
This study	Tropical	− 60.2 to 16.5 (mean = − 14.5)	− 10.0 to 475 (mean = 80.0)
Crawford et al. (2014)[a]	Temperate	− 200 to 25	90 to 325
Herreid et al. (2020)	Temperate	− 256.4 to 37.0 (mean = − 53.6)	18–635 (mean = 151)
Rocher-Ros et al. (2019)[a]	Arctic	− 90 to 5	− 5 to 175

[a]Ranges were not reported and thus range listed represents estimates from figures

greater availability of NO_3^- (McDowell et al. 1992). There is also evidence from a previous study in our study region (Potter et al. 2010) that denitrification proceeds to the most reduced end-product (N_2 over N_2O) more often in streams than in soils and that the relationship between total denitrification (mostly N_2) and aquatic N concentrations was strong. Studies assessing linkages between gas emissions from tropical forest soils and headwater streams found similar emissions of N_2O from both soils and streams, underscoring the potential landscape connection for N_2O dynamics in tropical systems (Potter et al. 2010; Barthel et al. 2022).

We also expected to see a negative relationship between dissolved O_2 and CO_2 due to the tradeoff between primary production and respiration, as has been identified in several studies (e.g., Crawford et al. 2014; Rocher-Ros et al. 2019; Herreid et al. 2020). The 1:1 line in Fig. 4 denotes this expected relationship under the assumption that aerobic metabolism produces the measured stream CO_2 concentrations. The majority of our data fall to the right of the 1:1 line, suggesting that other sources of CO_2 (i.e., anaerobic respiration, methane oxidation, or external inputs) contribute to the stream gas balance, consistent with other studies (e.g., Crawford et al. 2014; Herreid et al. 2020). In contrast to these other studies, and to sites globally, our range of dissolved O_2 is very narrow (Table 3) due to the high reaeration coefficients of these steep montane streams. This likely contributes to the lack of a significant relationship between CO_2 and O_2 at our sites.

In contrast to our results for N_2O and CO_2, we found that CH_4 concentrations were predictable by dissolved O_2 and varied with lithology (Figs. 3, 5) suggesting both biological and physical in-stream controls on CH_4 production. Higher concentrations of CH_4 are typically observed when O_2 becomes depleted due to the more reduced environment required for methanogenesis (Stanley et al. 2016). Sites underlain by quartz diorite had significantly higher CH_4 than sites in the volcaniclastic or mixed lithology watersheds (Fig. 3). We attribute this control to differences in streambed characteristics as well as differing soil conditions between lithologies. Particle sizes are remarkably different between lithologies, with volcaniclastic watersheds containing larger particles with a more uniform size distribution (Phillips and Jerolmack 2016) and quartz diorite watersheds containing smaller particles that are often sand-dominated yet more heterogenous (Pike et al. 2010, Supplementary Table 3). Providing both a source of organic matter and an anoxic environment, sediment deposition as well as the depth and supply of fine sediments have been shown to be important drivers of methanogenesis (Stanley et al. 2016; Bodmer et al. 2020; Herreid et al. 2020). The heterogeneity of quartz diorite stream beds may also drive the greater variability in CH_4 in these watersheds, as has been observed in water chemistry in previous studies (Wymore et al. 2019). This internal control of CH_4 production is consistent with another study in the tropics which found decoupling of aquatic CH_4 production from the terrestrial landscape and suggested the importance of production within benthic sediments or riparian zones (Barthel et al. 2022). Although the controls we discuss are related to CH_4 production, CH_4 oxidation may also be playing a role in the patterns we observed; however, our study was not designed to quantify the role of these two processes.

Concentrations and fluxes of greenhouse gases in a global context

Nitrous oxide concentrations in the Luquillo Mountains [1.1–46 nM (15–563% sat), mean = 13 nM (181% sat)] fall within the range of those reported

from other tropical and subtropical streams and rivers in sub-Saharan Africa (0.2–85.4 nM, mean = 9.2 nM, Borges et al. 2015; Upstill-Goddard et al. 2017; Marwick et al. 2018), southeast Asia (2.0–41.4 nM, Bange et al. 2019), and Australia (115–1430% sat, Andrews et al. 2021). Fluxes of N_2O, however, are much higher in the Luquillo Mountains relative to other tropical locations. Mean N_2O flux, as calculated from measured k, across the three streams was 194 µmol m^{-2} d^{-1} whereas African streams and rivers ranged from 1 to 67 µmol m^{-2} d^{-1} (Upstill-Goddard et al. 2017) and 2–16 µmol m^{-2} d^{-1} (Borges et al. 2015), and average fluxes reported from southeast Asia and subtropical Australia were ~ 25 µmol m^{-2} d^{-1} (Bange et al. 2019) and 4.01 ± 5.98 µmol m^{-2} d^{-1} (Andrews et al. 2021), respectively. Soued et al. (2016) estimated average N_2O flux from high latitudes (> 54°) as 1.7 µmol m^{-2} d^{-1}, 129 µmol m^{-2} d^{-1} from temperate streams and rivers (n = 133) and average tropical emissions of N_2O as 60.8 µmol m^{-2} d^{-1} (n = 15). Thus, our sites have emissions of N_2O that are higher than typical for tropical systems and are comparable to temperate streams. Contextualizing our N_2O concentrations and fluxes at both a tropical and global scale remains difficult due to the paucity of measurements.

Dissolved CH_4 concentrations from our study sites [0.006–3.03 µM (144–128,767% sat), mean = 0.22 µM (9.172% sat)] fall on the lower end of the global range [0–386 µM, mean = 1.35 µM; Stanley et al. (2016)]. Compared to other tropical studies, our CH_4 concentrations are comparable to those in Australia (0.19–62.13 µM, Atkins et al. 2017; 428–9450% sat, Andrews et al. 2021) and fall within the range and are often higher than streams and rivers in the Amazon basin (0.02–0.5 µM, Sawakuchi et al. 2014) and in Asia (0.0025–1.37 µM, Bange et al. 2019). Fluxes of dissolved CH_4 in our study using measured k ranged from − 0.05 to 24.71 mmol m^{-2} d^{-1} (mean = 1.79 mmol m^{-2} d^{-1}). In comparison with other tropical systems, our fluxes are higher than those of streams in rivers in Australia (0.04 mmol m^{-2} d^{-1}, Andrews et al. 2021), lower than those in Costa Rica (4.75 and 5.96 mmol m^{-2} d^{-1}, Oviedo-Vargas et al. 2015) and fall within the range of fluxes from the Amazon basin (0.01–40.30 mmol m^{-2} d^{-1}, Sawakuchi et al. 2014). Globally, fluxes from the Luquillo streams fall within the range reported by Stanley et al. (2016) (< 1–40.49 mmol m^{-2} d^{-1}) but on average are lower than the global mean (4.23 mmol m^{-2} d^{-1}). It is important to note that our CH_4 fluxes only represent diffusive emissions. Ebullitive CH_4 fluxes can be substantial and often higher than diffusive fluxes (e.g., Zheng et al. 2022), and thus our flux estimates are a conservative estimate of total CH_4 flux.

Concentrations of CO_2 in the Luquillo Mountains [3.4–487 µM (29–4238% sat), mean = 90 µM (791% sat)] are lower than the average reported for two streams in Costa Rica (mean = 580 µM, Oviedo-Vargas et al. 2015) and within the range reported for Australian streams (520–1640% sat, Andrews et al. 2021). Mean CO_2 flux from our streams (1.84 mol m^{-2} d^{-1}) was higher than both the global average reported by Lauerwald et al. (2015) for streams and rivers (0.46 mol C m^{-2} d^{-1}) as well as for small tropical streams (0.65 mol C m^{-2} d^{-1}). However, there are more recent tropical studies reporting higher fluxes (e.g., 74 mol m^{-2} d^{-1}, Andrews et al. 2021).

Differences between fluxes observed in Luquillo streams and other tropical sites could be due to differences in precipitation, topography, and the well-documented role that lithology plays across this mountainous landscape. The steep topography alone results in larger reaeration values than would be observed in flatter tropical landscapes, which could be a reason why we see much higher fluxes of N_2O even when dissolved concentrations are comparable to other tropical sites. The relatively consistent precipitation patterns in Puerto Rico (McDowell et al. 2012), compared with tropical regions having distinct wet/dry seasons, along with the proposed riparian production of N_2O and CO_2, may also explain some of the variability between Luquillo streams and other tropical streams.

Flux estimates using measured versus modeled k

Many studies use a modelling approach (e.g., equations in Raymond et al. 2012) to estimate gas transfer velocities when obtaining field reaeration measurements is not feasible. However, large differences in flux estimations can be observed when calculating fluxes from both measured and modeled k. Differences were particularly evident at the quartz diorite site (RI), where average fluxes for all three gases were more than 57 times larger using modelled k than when using measured k (Table 2). These large differences in fluxes between the two methods of determining k are a result of the negative relationship between k and

discharge that was determined through field-based measurements of reaeration at RI. We trust this negative relationship because flow becomes more laminar and less turbulent during high discharge events at this site (RI), and it is common to observe decreases in k with increasing discharge (Aristegi et al. 2009). Although fluxes using modelled k were higher at RI and QP compared with measured k, they were lower at QS likely because of the steep stream slope at this site. Modelling approaches have been shown to be inadequate for turbulent streams with steep slopes (Hall Jr. and Madinger 2018), likely explaining the underestimation at QS. The field-based approach to determine k and ultimately calculate flux can account for geomorphological nuances that are missed using a modelling approach. Using the modelled approach alone in our study would have resulted in a significant overestimation of fluxes for all three GHGs at RI particularly. Future studies should consider whether there are unique geomorphological aspects of their study watersheds that could make modelled approaches less accurate.

In the Luquillo Mountains, stream CO_2 and N_2O concentrations appear connected to terrestrial inputs, while CH_4 concentrations are driven by internal controls (i.e., O_2 availability and sediment characteristics). The lack of coherence surrounding controls and patterns among the three gases underscores the importance of considering the role of landscape heterogeneity. Whether or not our fluxes are higher or lower than other tropical streams varies among gases, challenging our ability to ascertain the role of tropical streams and rivers in fluvial emissions on a global scale. Increased direct, long-term, and high-quality greenhouse gas measurements and estimates of k from a more diverse range of tropical ecosystems are needed to further elucidate the drivers and fluxes of GHGs from fluvial tropical ecosystems, and ultimately to determine if the tropics are hotspots of emissions for all three gases.

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Data availability The datasets used for this study are available for public use: http://www.hydroshare.org/resource/04f8de6f4da8482185212919 34f06eba.

Declarations

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

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