

*p*CO₂ and DOC
temperature-
dependence in
lakes

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Temperature-dependence of the relationship between *p*CO₂ and dissolved organic carbon in lakes

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Abstract

The relationship between the partial pressure of carbon dioxide ($p\text{CO}_2$) and dissolved organic carbon (DOC) concentration in Brazilian lakes, encompassing 225 samples across a wide latitudinal range in the tropics, was tested. Unlike the positive relationship reported for lake waters, which was largely based on temperate lakes, we found no significant relationship for tropical and subtropical Brazilian lakes, despite very broad ranges in both $p\text{CO}_2$ and DOC. Closer examination showed that the strength of $p\text{CO}_2$ vs. DOC relationships declines with increasing water temperature, suggesting substantial differences in carbon cycling in warm lakes, which must be considered when upscaling limnetic carbon cycling to global scales.

1 Introduction

Lakes cover less than 2 % of the continent's surface (Downing et al., 2006; McDonald, 2012), but play a significant role in the global carbon (C) cycle (Cole et al., 1994, 2007; Tranvik et al., 2009), contributing significantly to C burial and emissions to the atmosphere (Cole et al., 2007; Downing et al., 2008 and Tranvik et al., 2009). Dissolved organic carbon (DOC) represents a major C pool in lakes, with both autochthonous and allochthonous contributions (Xenopoulos et al., 2003; Duarte and Prairie, 2005; Duarte et al., 2005; Sobek et al., 2005; Cole et al., 2007; Prairie 2008; Marotta et al., 2009; Tranvik et al., 2009; Larsen et al., 2012), supporting heterotrophy and primary productivity (Sobek et al., 2007) and affecting key biological and physico-chemical processes involved in C cycling (Steinberg et al., 2006). Large inputs of terrestrial organic C and its subsequent mineralization have been suggested to be a major driver of CO_2 supersaturation commonly encountered in lakes (Xenopoulos et al., 2003; Duarte and Prairie, 2005; Duarte et al., 2005; Sobek et al., 2005; Cole et al., 2007; Prairie, 2008; Marotta et al., 2009; Larsen et al., 2012).

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The mechanistic connection between DOC and heterotrophic CO_2 production is believed to underpin the significant positive relationship between $p\text{CO}_2$ and DOC reported in comparative analyses (Houle, 1995; Sobek et al., 2005; Larsen et al., 2012). However, recent analyses have revealed that the relationship between $p\text{CO}_2$ and DOC in lake waters is regionally variable and not universal (Lapierre and del Giorgio, 2012). Hence, relationship between $p\text{CO}_2$ and DOC reported in comparative analyses based on data sets dominated by temperate and high-latitude lakes may not be extrapolated to tropical lakes.

At low latitudes, warm conditions over the whole year may impose intrinsically faster rates of C cycling in terrestrial (Ometto et al., 2005) and aquatic (Marotta et al., 2009, 2010) ecosystems compared to the low rates characteristic of temperate systems in winter. High temperatures affect heterotrophic activity and the associated mineralization rates of organic matter in soils (Davidson et al., 2006), waters (López-Urrutia et al., 2007; Wohlers et al., 2008; Regaudie-de-Gioux and Duarte, 2012) and aquatic sediments (Wadham et al., 2012; Gudasz et al., 2010; Marotta et al., 2014). An enhanced heterotrophic activity in tropical ecosystems would support high fluxes of CO_2 , leading to CO_2 enrichment in lake waters through inputs from inflowing waters and mineralization processes in the water column and sediments.

A previous comparative analysis, also characterized by a paucity of low latitude data, reported $p\text{CO}_2$ in lake waters to be independent of temperature (Sobek et al., 2005). However, a positive relationship between temperature and $p\text{CO}_2$ was observed when subtropical and tropical ecosystems were included in the analysis (Davidson et al., 2004; Marotta et al., 2009; Dillon et al., 2010). Hence, the relationship between lake $p\text{CO}_2$ and DOC could also be temperature-dependent and, therefore, may differ between temperate and tropical lakes. Here, we test the applicability of the relationship between $p\text{CO}_2$ and DOC, largely derived from north-temperate lakes (Houle, 1995; Sobek et al., 2005; Larsen et al., 2012), to tropical and subtropical lakes in Brazil. Brazil has a large territory in the tropics, showing a high density of lakes and ponds

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pH, salinity and temperature in waters were measured in situ. pH was determined using a pH meter (Digimed – DM2) with a precision of 0.01 calibrated with standard solutions of 4.0 and 7.0 units of pH before each sampling hour. Temperature and salinity were measured using a Thermosalinometer (Mettler Toledo – SevenGo SG3) coupled to a probe inLab 737 previously calibrated with 0.01 M KCl. Surface lake waters for total alkalinity and DOC analyses were collected taking care to avoid bubbles at about 0.5 m of depth using a 1 L Van Dorn bottle. Alkalinity was determined in the field by the Gran's titration with 0.0125 M HCl immediately after sampling (Stumm and Morgan, 1996). Water samples for DOC were pre-filtered (0.7 mm, Whatman GF/F) and preserved by acidification with H_3PO_4 85 % to reach $\text{pH} < 2.0$ in sealed glass vials (Spyres et al., 2000). In the lab, DOC was determined by high-temperature catalytic oxidation using a TOC-5000 Shimadzu Analyzer. $p\text{CO}_2$ concentrations in surface waters were calculated from pH and alkalinity following Weiss (1974), after corrections for temperature, altitude and ionic strength according to Cole et al. (1994).

Additional statistical analyses were doing assuming corrections of $[\text{HA}] = [\text{DOC}] / 8.33$ in the alkalinity to correct the calculated $p\text{CO}_2$ for the contribution of organic acids, after Wang et al. (2013). This correction lead, a change of non-significant relationship between $p\text{CO}_2$ and DOC for a negative significant relationship (slope = -16.8 ± 52.5 ; $p < 0.05$).

2.3 Statistical analyses

The variables $p\text{CO}_2$ and DOC did not meet the assumptions of parametric tests even after logarithmic transformations (Zar, 1996), as data were not normally distributed (Kolmogorov-Smirnov, $p < 0.05$) and variances were heterogeneous (Bartlett, $p > 0.05$). Therefore, we used medians and non-parametric tests to compare these variables among biomes (Kruskall-Wallis followed by Dunn's multiple comparison post hoc test, $p < 0.05$). Relationships between $p\text{CO}_2$ and DOC were assessed using the non-parametric Spearman correlation for raw data, but linear regression equations were fitted for log-transformed to compare our results with previous studies (significance level

(1255–35 278 μatm ; Marotta et al., 2009), reservoirs (1840 μatm ; Aufdenkampe et al., 2011) and wetlands (3080–6170 μatm ; Aufdenkampe et al., 2011).

In contrast to previous reports (Sobek et al., 2005), we found no relationship, or a weak negative one, between $p\text{CO}_2$ and DOC in Brazil lakes. Contrasting results between low and high latitude lakes show that consistent positive $p\text{CO}_2$ -DOC relationships from data sets strongly dominated by temperate lakes (Houle, 1995; Prairie et al., 2002; Jonsson et al., 2003; Sobek et al., 2005; Roehm et al., 2009; Lapiere and del Giorgio, 2012; Larsen et al., 2012) cannot be extrapolated to tropical lakes. The results presented show that tropical lakes range widely in $p\text{CO}_2$, reaching very high values, but tend to have comparatively more uniform DOC concentrations. Moreover, previous research demonstrated a relationship between $p\text{CO}_2$ and water temperature across lakes (Marotta et al., 2009).

Further analysis, by pooling our data onto a global dataset showed the relationship between $p\text{CO}_2$ and DOC in lake waters to be temperature-dependent, with lakes with colder waters characterized by strong relationships and warm-water, tropical lakes, showing no relationship. These results point at temperature-dependence of carbon cycling in lakes. Temperature is a master variable affecting metabolic processes (Brown et al., 2004), and the efficiency of organic mineralization for a given organic carbon pool (Gudasz et al., 2010; Kosten et al., 2010; Marotta et al., 2009, 2014; Wadham et al., 2012). The temperature-dependence of organic matter cycling is, however, dependent on their factors, such as the refractory nature of the organic matter available (Davidson et al., 2006) and/or nutrient availability (Lopez-Urrutia and Moran, 2007), comparing different sites or ecosystems. Previous results have revealed a contrasting pattern of regulation where bacterial respiration is temperature-dependent, whereas production is regulated by nutrient availability in warm ocean waters (Lopez-Urrutia and Moran, 2007). Consistent reports have supported large-scale regional differences in C delivery, quality, and in lake-processing (Roehm et al., 2009; Lapiere and Del Giorgio, 2012), which may blur any general positive relationship between $p\text{CO}_2$ -DOC previously for global lakes (Sobek et al., 2005).

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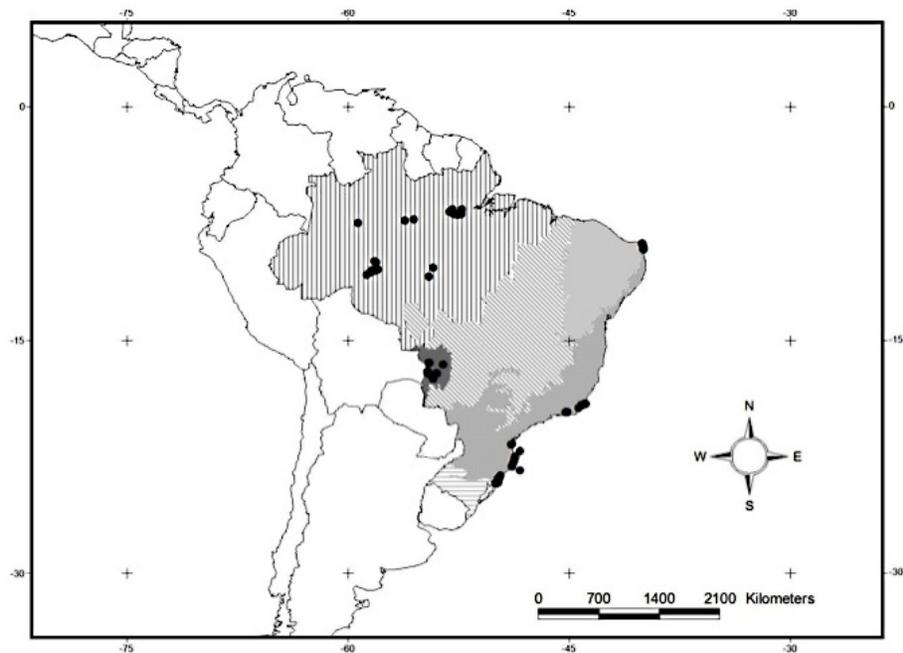


Figure 1. Geographic location of Brazilian lakes sampled at different biomes (IBGE 2004, available in ftp://geoftp.ibge.gov.br/mapas_tematicos/mapas_murais/biomas.pdf): Amazonia Forest (vertical lines), Pantanal Floodplain (dark gray), and Atlantic Forest (gray; Tropical and Subtropical coastal lakes).

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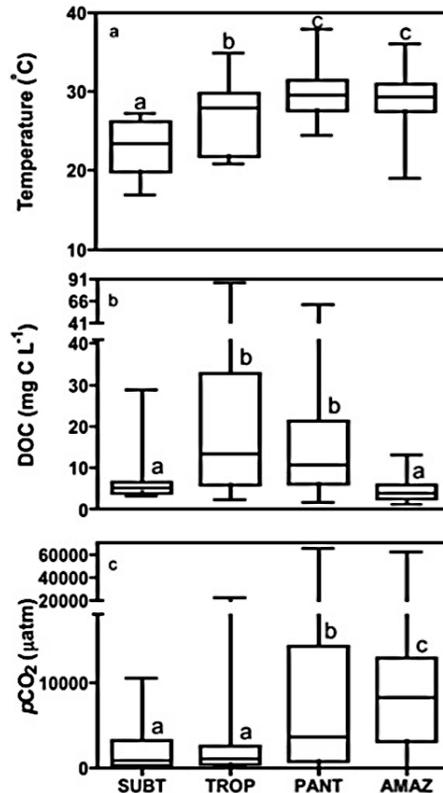


Figure 2. Values of (a) temperature (°C), (b) DOC concentrations (mg C L⁻¹) and (c) pCO₂ concentration (µatm) from different biomes, as defined by (SUBT) Subtropical Coastal lakes ($n = 37$), (TROP) Tropical coastal lake ($n = 63$), (PANT) Pantanal Floodplain ($n = 58$) and (AMAZ) Amazonia Forest ($n = 67$). The line depicts the median. The boxes show the quartiles, and the whiskers mark the 10 and 90% percentiles. Different lowercase letters near the boxplot indicate significant statistic differences between the groups (Kruskall-Wallis followed by Dunn's multiple comparison post hoc test, $p < 0.05$).

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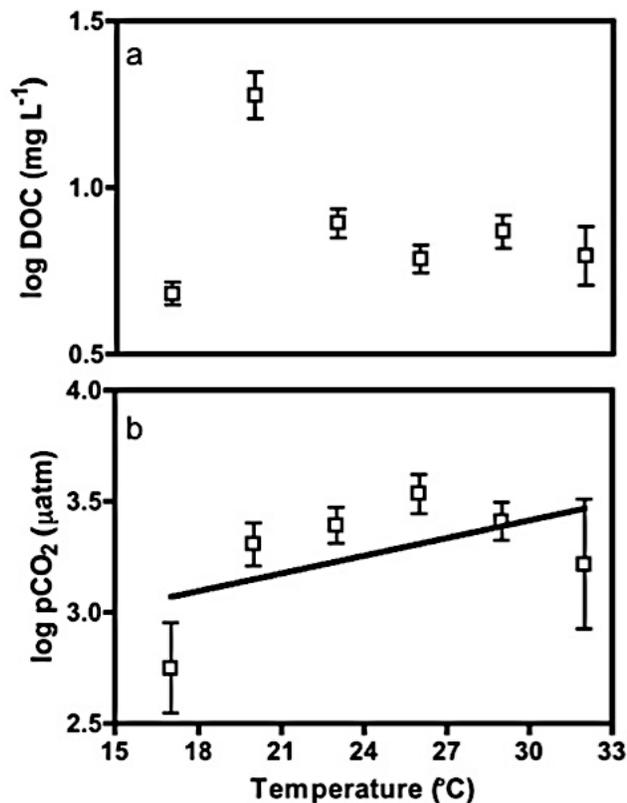


Figure 3. The linear relationship between the mean (\pm SE) of Brazilian lakes: **(a)** DOC (mg CL^{-1}) and **(b)** $p\text{CO}_2$ (μatm) of lakes, grouped by 3°C temperature bins of water temperature ($^\circ\text{C}$). The linear regression between DOC (mg CL^{-1}) and temperature bins was not significant; ($p > 0.05$), while those for the $p\text{CO}_2$ was significant ($y = 357.1 \pm 80.11x + -5649 \pm 2005$; $R^2 = 0.83$, $F = 19.87$; $p < 0.05$).

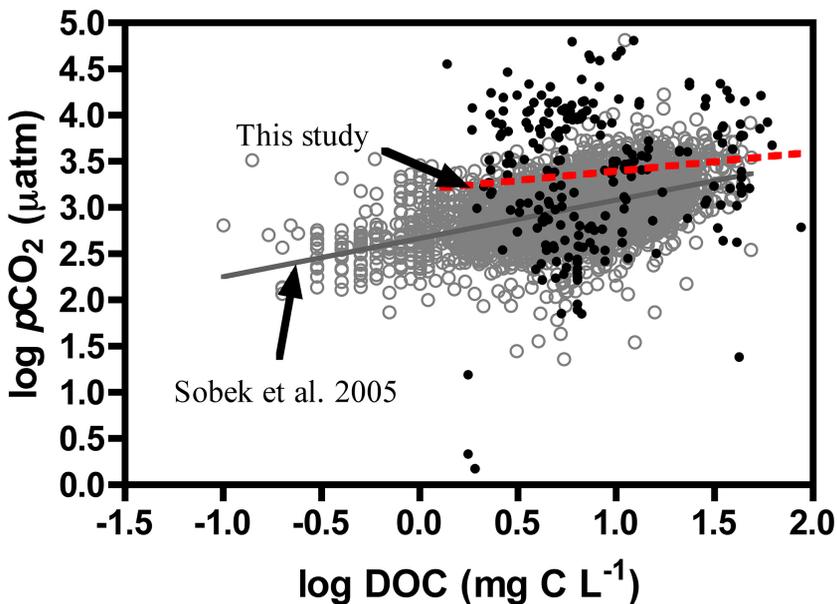


Figure 4. Comparisons of $p\text{CO}_2$ against DOC concentrations for lakes from this study (black circles) and from Sobek et al. (2005) (grey circles). Each point in the plot represents one measurement. Dashed line represents the linear regression for all Brazilian data points (not significant; $p > 0.05$), while the solid line represented the linear regression from Sobek et al. (2005) ($\log p\text{CO}_2$ (μatm) = $2.67 + 0.414 \log \text{DOC}$ (mg C L^{-1}); $R^2 = 0.26$; $p < 0.05$).

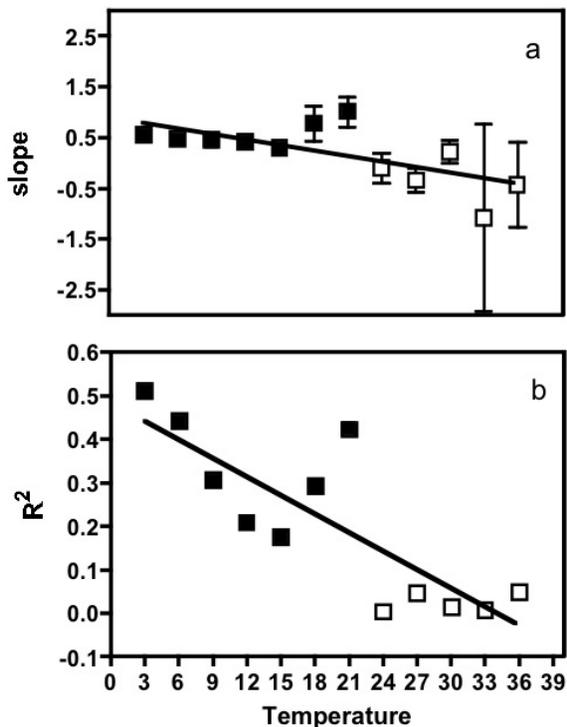


Figure 5. The figure represents the linear regression between **(a)** slope (\pm SE) and **(b)** R^2 and lake surface waters (significant $p < 0.05$) grouped by 3° temperature bins. The full and open squares represent respectively significant ($p < 0.05$) and non-significant ($p > 0.05$) linear regressions between absolute values of $p\text{CO}_2$ and DOC concentrations for each bin interval (n varying from 7 and 1540). The solid lines represent both fitted regression equation encompassing all bins. Linear Slope ($y = -0.04 \pm 0.01x + 0.91 \pm 0.28$ temperature 3° bin; $R^2 = 0.46$; $F = 8.45$; $p < 0.05$, and linear R^2 ($y = -0.01 + 0.48 \pm 0.07$ temperature 3° bin; $R^2 = 0.69$; $F = 21.9$; $p < 0.05$).

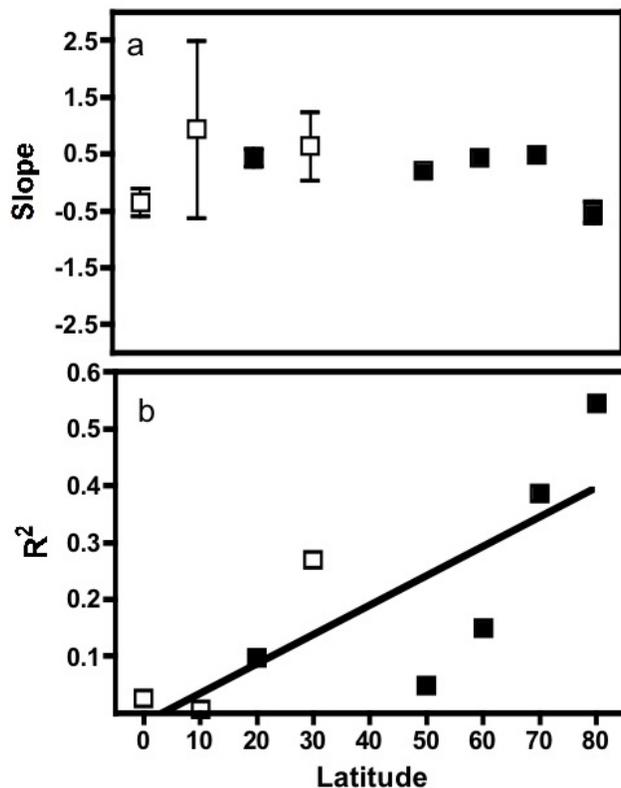


Figure 6. The figure represents the linear regression between **(a)** slope (\pm SE), not significant and **(b)** R^2 , significant ($p < 0.05$) and latitude, grouped by 10° latitude bins. The full and open squares represent respectively significant ($p < 0.05$) and not significant ($p > 0.05$) linear regression for each bin interval. The solid line represents the linear regression encompassing all bins. Linear Slope was not significant ($p > 0.05$) and Linear $R^2(y) = 0.005 \pm 0.001x + (-0.02 \pm 0.08)$ latitude 10° bin; $R^2 = 0.61$; $F = 9.47$ ($p < 0.05$).