Temperature-dependence of the relationship between $pCO_2$ and dissolved organic carbon in lakes

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Abstract

The relationship between the partial pressure of carbon dioxide ($p$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 $p$CO$_2$ and DOC. Closer examination showed that the strength of $p$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 tactility (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).
The mechanistic connection between DOC and heterotrophic CO$_2$ production is believed to underpin the significant positive relationship between $p$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 $p$CO$_2$ and DOC in lake waters is regionally variable and not universal (Lapiere and del Giorgio, 2012). Hence, relationship between $p$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 $p$CO$_2$ in lake waters to be independent of temperature (Sobek et al., 2005). However, a positive relationship between temperature and $p$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 $p$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 $p$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...
(Downing et al., 2006), with a diversity of conditions that render them appropriate to examine general patterns (e.g. Marotta et al., 2009).

2 Methods

2.1 Study area and lakes

Brazil extends from 5°16’20” North to 33°44’42” South, showing an area of approximately 8,547,000 km² that represents half of South America and encompasses a high diversity of low-latitude landscapes (Ab’Saber, 2003) predominantly located within tropical latitudes. We conducted a survey of $p$CO$_2$ and DOC between 2003 and 2011 in surface waters of 166 permanent lakes from 0 to 33° of latitude across Brazil (Fig. 1), yielding a total of 225 water samples. The lakes were sampled in representative biomes of Brazil: (1) Amazonia Forest (Amazonia Biome, $n = 65$), (2) Pantanal Floodplain (Pantanal Biome, $n = 29$) and the (3) Tropical (<24° of latitude) and (4) Subtropical (>24° and <33° of latitude) Coasts, both in the Atlantic Forest Biome ($n = 35$ and $n = 37$ lakes, respectively; Fig. 1). These biomes follow the classification of the Brazilian Institute of Geography and Statistics for biomes (IBGE 2004, ftp://geoftp.ibge.gov.br/mapas_tematicos/mapas_murais/biomas). Our data set encompasses a broad inter-lake heterogeneity ($n = 166$) for $p$CO$_2$ and DOC simultaneously sampled among Brazilian biomes and along the latitudinal gradient, independent of the year’s season.

The Amazonia Forest biome is formed by the most extensive hydrographic network of the globe, the Amazon River basin that occupies a total area about 6.11 million km² from its headwaters in the Peruvian Andes to the mouth in the Atlantic Ocean (ANA – www.ana.gov.br). The Amazon Forest is the Brazilian biome characterized by higher mean annual precipitation (approximately 2200 mm) coupled to warm mean air temperatures around 25°C and high cloud coverage and humidity with low fluctuations over the whole year (Chambers, 1999). We sampled a wide variety of lakes, characteristic
of different areas of the Amazonian Forest, encompassing “clear” (low DOC and suspended solids), “white” (low DOC and high suspended solids) and “dark” (high DOC and low suspended solids) lakes.

The Pantanal Floodplain is the world’s largest tropical freshwater wetland, extending across an area of about 150,000 km$^2$ between 16 and 20° S and 58 and 55° W (Por, 1995). The annual averages temperature and precipitation are approximately 22°C and 1000 mm, respectively (Mariot et al., 2007), with a strong seasonality and subsequent variation in the flooded area (Junk and Nunes da Cunha, 2005). The high-water period occurs during the rainy summer (usually from September to December), and low waters typically during the dry winter (from March to July; Hamilton, 2002).

The Atlantic Forest biome extends along a broad latitudinal belt between 5 and 30° S from subtropics to tropics and a narrow longitudinal section between 55 and 56° W, occupying an area of 1.11 million km$^2$ along the Brazilian coast (IBGE – www.ibge.gov.br). This biome is characterized by numerous shallow coastal lakes receiving high inputs of refractory organic matter (Farjalla et al., 2009) derived from the typical open xerophytic vegetation on sandy soils, where water retention is low (Scarano, 2002). The mean air temperatures vary from 27°C in winter to 30°C in summer at the tropical coast (< 24° of latitude; Chellappa et al., 2009) and from 17 and 20°C at the subtropical coast (> 24° of latitude; Waechter, 1998). The mean annual precipitation reaches 1164 mm (Henriques et al., 1986) and 1700 mm (Waechter, 1998) in the tropical and subtropical Brazilian coast respectively. This biome is also characterized by strong seasonality, with rainy summers and dry winters (Chellappa et al., 2009).

### 2.2 Sampling design and analytical methods

We sampled 166 lakes collecting 4 to 5 samples over 24 h at each lake. The values reported here represents daily averages for $\rho$CO$_2$ and two replicate samples in a given day hour for DOC concentrations. The lakes were sampled, on an opportunistic manner, in both dry and rainy seasons (87 % Amazonia, 16 % Pantanal, 74 % Tropical costs, 100 % Subtropical coast, in dry season, respectively).
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$_3$PO$_4$ 85% to reach 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. $p$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 $[HA] = [DOC] / 8.33$ in the alkalinity to correct the calculated $p$CO$_2$ for the contribution of organic acids, after Wang et al. (2013). This correction lead, a change of non-significant relationship between $p$CO$_2$ and DOC for a negative significant relationship (slope $= -16.8 \pm 52.5; p < 0.05$).

### 2.3 Statistical analyses

The variables $p$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 $p$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...
set at \( p < 0.05 \). To test the temperature-dependence of the relationship between \( p\text{CO}_2 \) and DOC we pooled the lakes in our survey with those in the database from Sobek et al. (2005) and fitted linear relationships between \( p\text{CO}_2 \) and DOC, both log-transformed, for lakes grouped by 3°C temperature bins. We also tested the latitudinal dependence of the relationship between \( p\text{CO}_2 \) and DOC concentration by fitting linear relationships to lakes in the pooled data set grouped by 10° latitude bins. Statistical analyses were performed using the software Graphpad Prism version 4.0 for Macintosh (GraphPad Software, San Diego, CA).

### 3 Results

The lake waters surveyed were warm across all biomes (median 25–75% interquartile range = 27.5°C, 25.2–30.1), but colder in subtropical coastal lakes (23.4°C, 20.0–26.2) compared to Pantanal and Amazonian lakes (29.5°C, 27.7–31.4 and 29.4°C, 27.6–31.0, respectively; Dunn’s test, \( p < 0.05 \), Fig. 2a). DOC concentrations were consistently high (6.3 mg C L\(^{-1}\), 4.3–11.9) for all Brazilian biomes, but significant lower in the Amazonian Forest (3.8 mg C L\(^{-1}\), 2.7–5.8) compared to the tropical coast (13.4 mg C L\(^{-1}\), 6.1–32.8; Fig. 2b; Dunn’s test, \( p < 0.05 \)). Most \( p\text{CO}_2 \) lakes (approximately 83%) showed surface waters supersaturated in CO\(_2\) relative to atmospheric equilibrium (390 µatm), with much higher \( p\text{CO}_2 \) values in Amazonian lakes (7956 µatm, 3033–11346) compared to subtropical coastal lakes (900 µatm, 391.3–3212; Fig. 2c; Dunn’s test, \( p < 0.05 \)). DOC concentrations, grouped in 3°C temperature bins, was independent of temperature, whereas there \( p\text{CO}_2 \) increased significantly with temperature \((p < 0.05, R^2 = 0.83; \text{Fig. 3a and b})\).

The \( p\text{CO}_2 \) in surface waters of Brazilian lakes was independent of DOC concentrations (Spearman correlation for raw data and linear regression for log-transformed data, \( p > 0.05 \), Fig. 3). Correcting \( p\text{CO}_2 \) values corrected for the potential interference of organic acids resulted in a minor change in \( p\text{CO}_2 \), showing a negative relationship after this correction (slope = \(-116.8 \pm 52.5; p < 0.05 \)). Fitting the linear regression between
$pCO_2$ and DOC in Brazilians dates was fitted using the values of $pCO_2$ corrected for the influence of organic acids resulted in a very weak significant, but negative, relationship ($R^2 = 0.1$, $p < 0.05$) between $pCO_2$ and DOC. The range of $pCO_2$ for a given DOC in Brazilian lakes was larger than that reported by Sobek et al. (2005) for data set dominated by high-latitude cold lakes, despite the number of lakes in their data set being much larger.

The contrast between the positive relationship between $pCO_2$ and DOC concentration in the, largely temperate, data set of Sobek et al. (2005) and the lack or weak negative relationship in Brazil lakes suggest that the relationship may be temperature dependent, as $pCO_2$ increased with temperature in Brazilian lakes but DOC did not (Fig. 4). We tested the temperature-dependence of the relationship between $pCO_2$ and DOC concentration by pooling both data sets and examining the strength of $pCO_2$ vs. DOC relationships for lakes grouped within temperature and latitude bins. This analysis showed a significant decline in the strength of the (log-log) $pCO_2$ vs. DOC relationships, as reflected in declining slopes ($p < 0.05$) and $R^2$ with increasing temperature (Fig. 5). In contrast, the slopes of (log-log) $pCO_2$ vs. DOC relationships, for lakes grouped within 10° latitude bins, did not change significantly with latitude ($p > 0.05$) although the corresponding $R^2$ increased with increasing latitude ($p < 0.05$; Fig. 6).

4 Discussion

The Brazilian lakes sampled here were characterized by a prevalence of CO$_2$ supersaturation, consistent with general trends for lakes (e.g. Cole et al., 1994; Algesten et al., 2005) and earlier reports for tropical lakes (Marotta et al., 2009). The very high $pCO_2$ values observed here (900–8300 µatm) are consistent with those reported earlier for the Amazon River and tributaries (2000–12 000 µatm; Richey et al., 2002), Amazon floodplain lakes (3000–4898 µatm; Rudorff et al., 2012), Pantanal lakes and wetlands (2732–10 620 µatm; Hamilton et al., 1995), coastal lakes (768–9866 µatm; Kosten et al., 2010; 361–20 037 µatm; Marotta et al., 2010b), and global values for tropical lakes...
(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 \( pCO_2 \) and DOC in Brazil lakes. Contrasting results between low and high latitude lakes show that consistent positive \( pCO_2 \)-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 \( pCO_2 \), reaching very high values, but tend to have comparatively more uniform DOC concentrations. Moreover, previous research demonstrated a relationship between \( pCO_2 \) and water temperature across lakes (Marotta et al., 2009).

Further analysis, by pooling our data onto a global dataset showed the relationship between \( pCO_2 \) 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 \( pCO_2 \)-DOC previously for global lakes (Sobek et al., 2005).
In conclusion, the finding that $pCO_2$ does not increase with DOC concentration in Brazilian tropical lakes rejects the hypothesis that DOC serves as a universal predictor for $pCO_2$ in lake waters (Larsen et al., 2012). The analysis of a global data set provides evidence that the strength of the increase in $pCO_2$ with increasing DOC concentration declines at increasing temperature. Therefore, our results suggest potentially important latitudinal implications from depositional aquatic environments, whose causes still need to be better addressed to improve accuracy of global C cycle models.

Author contributions. All authors contributed to the study design, interpreted data and wrote or commented the manuscript. L. Pinho and H. Marotta performed the sampling and sample analyses.

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References


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 costal lakes).
Figure 2. Values of (a) temperature (°C), (b) DOC concentrations (mg C L⁻¹) and (c) $p$CO₂ 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, $p < 0.05$).
Figure 3. The linear relationship between the mean (±SE) of Brazilian lakes: (a) DOC (mg C L$^{-1}$) and (b) $\rho$CO$_2$ (µatm) of lakes, grouped by 3°C temperature bins of water temperature (°C). The linear regression between DOC (mg C L$^{-1}$) and temperature bins was not significant; ($p > 0.05$), while those for the $\rho$CO$_2$ was significant ($y = 357.1 ± 80.11x + -5649 ± 2005; R^2 = 0.83, F = 19.87; p < 0.05$).
Figure 4. Comparisons of $pCO_2$ 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) ($\log pCO_2$ (µatm) = 2.67 + 0.414 log DOC (mg C L$^{-1}$); $R^2 = 0.26; p < 0.05$).
Figure 5. The figure represents the linear regression between (a) slope (±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 absolutes values of $pCO_2$ 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; $R^2 = 0.69; F = 21.9; p < 0.05$. 

\[ y = -0.04 \pm 0.01x + 0.91 \pm 0.28 \]
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Figure 6. The figure represents the linear regression between (a) slope (±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 $R^2(y) = 0.005 ± 0.001x + (−0.02 ± 0.08)$ latitude 10° bin; $R^2 = 0.61; F = 9.47 (p < 0.05)$. 